

Quality Assurance Project Plan

Mobile Laboratory Program

Revision 3



City of Houston

Bureau of Pollution Control and Prevention

**7411 Park Place Boulevard
Houston, Texas 77087**

March 2011

A. PROJECT MANAGEMENT

A1. Title and Approval Sheet

A1.a. Quality Assurance Project Plan Identification

Document Title: Quality Assurance Project Plan for the Mobile Laboratory Program

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A1.b Approval and Concurrence

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Appendix A: Responsibilities and Authorities of Personnel in Quality Assurance

Appendix B: References

Appendix C: Standard Operating Procedure - TD-GC/FID/MS

DRAFT

A3. Distribution List

The following individuals/organizations will receive copies of the approved Quality Assurance Project Plan (QAPP) for the Mobile Laboratory Program (MLP) to measure air toxics in the Houston Ship Channel (HSC) Area.

City of Houston Bureau of Pollution Control and Prevention (BPCP):

Arturo J. Blanco – Bureau Chief, BPCP

Donald Richner - Program Manager, MLP; Environmental Analyst - BPCP

James Rhubottom, Jr. – Operations Leader and Chemist, MLP

Youjun Qin – Data Modeler and Chemist, MLP

Peter Chen – Quality Assurance Officer and Chemist, MLP

U.S. Environmental Protection Agency (EPA)

Aunjane' E. Gautreaux, Project Officer, U.S. EPA, Region 6

Kuenja Chung, Ph.D., Air Toxics Project Lead, U.S. EPA, Region 6

The Multimedia Special Initiatives Section maintains a distribution list of the Quality Assurance (QA) files at the City of Houston Bureau of Pollution Control and Prevention. The QA Officer verifies the QAPP distribution list on an annual basis with updates distributed as necessitated by revisions to the QAPP.

A. PROJECT MANAGEMENT

A4. Project/Task Organization

This QAPP describes the work to measure air toxics in the HSC area performed by the MLP staff for the City of Houston (COH) Department of Health and Human Services (DHHS), Bureau of Pollution Control and Prevention (BPCP), Technical Services Division as specified under the Agreement XA-96620501-0.

BPCP has four comprising sections, specifically, Multimedia Special Initiatives (MSI), Administration, Multimedia Response and Assistance (MRA), and Technical Services (TSS) with section chiefs reporting to the Bureau Chief. The Bureau Chief reports to the Assistant Director of Environmental Health who in turn reports to the DHHS Director. The Director of HDHHS reports to the Mayor. Figure 1 details the HDHHS organizational chart while figure 2 denotes the BPCP organizational chart. Figure 3 reflects the MLP organizational chart. Figure 4 shows the regulatory relationship as it pertains to the MLP.

Technical Services monitors ambient air quality in the City of Houston. The data documents air quality trends within the city, including events in exceedance of the National Ambient Air Quality Standards (NAAQS).

The primary responsibility of MLP team within the Multimedia Special Initiatives Section lies in maintaining and operating the Mobile Ambient Air Monitoring Laboratory (MAAML) including all required calibration and quality assurance/quality control (QA/QC) protocols. MLP management assures that the instruments, personnel, methods, QC procedures, and records conform to the MLP Quality Management Plan, MLP Quality Assurance Project Plan, MLP Standard Operating Procedures (SOPs) as well as all applicable city, state, and federal guidelines. Each team member has certain responsibilities to fulfill for the QA/QC program to be successful.

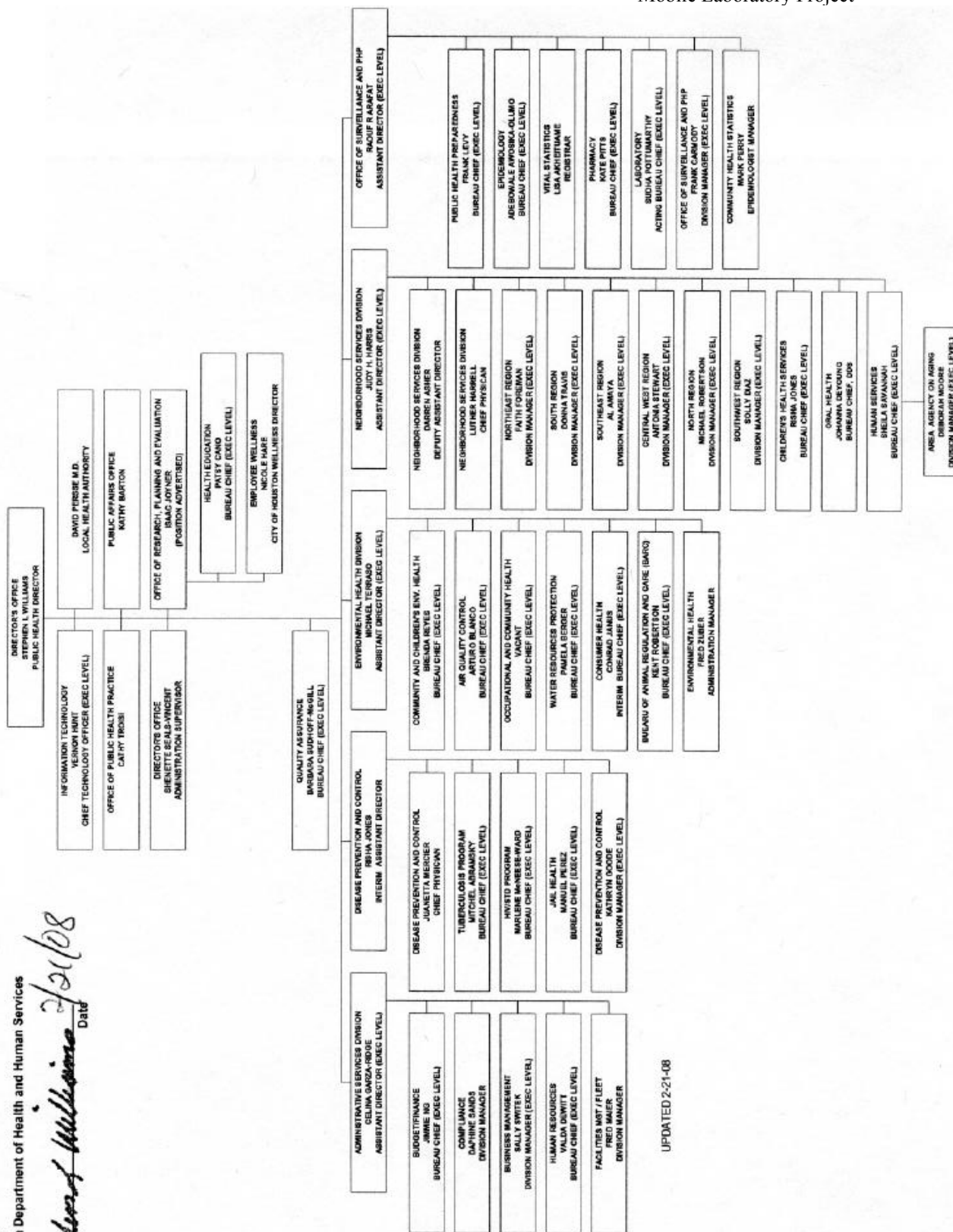
The document entitled "COH Responsibilities and Authorities of Personnel" in Appendix A defines the roles and responsibilities of individuals involved in QA management for the MLP.

HOUSTON DEPARTMENT OF HEALTH AND HUMAN SERVICES

DIRECTOR'S OFFICE

Stephen L. Williams, M.Ed., MPA
Director
Houston Department of Health and Human Services

Stephen L. Williams
Date: 2/20/08



UPDATED 2-21-08

Figure 1: HDHHS organization chart

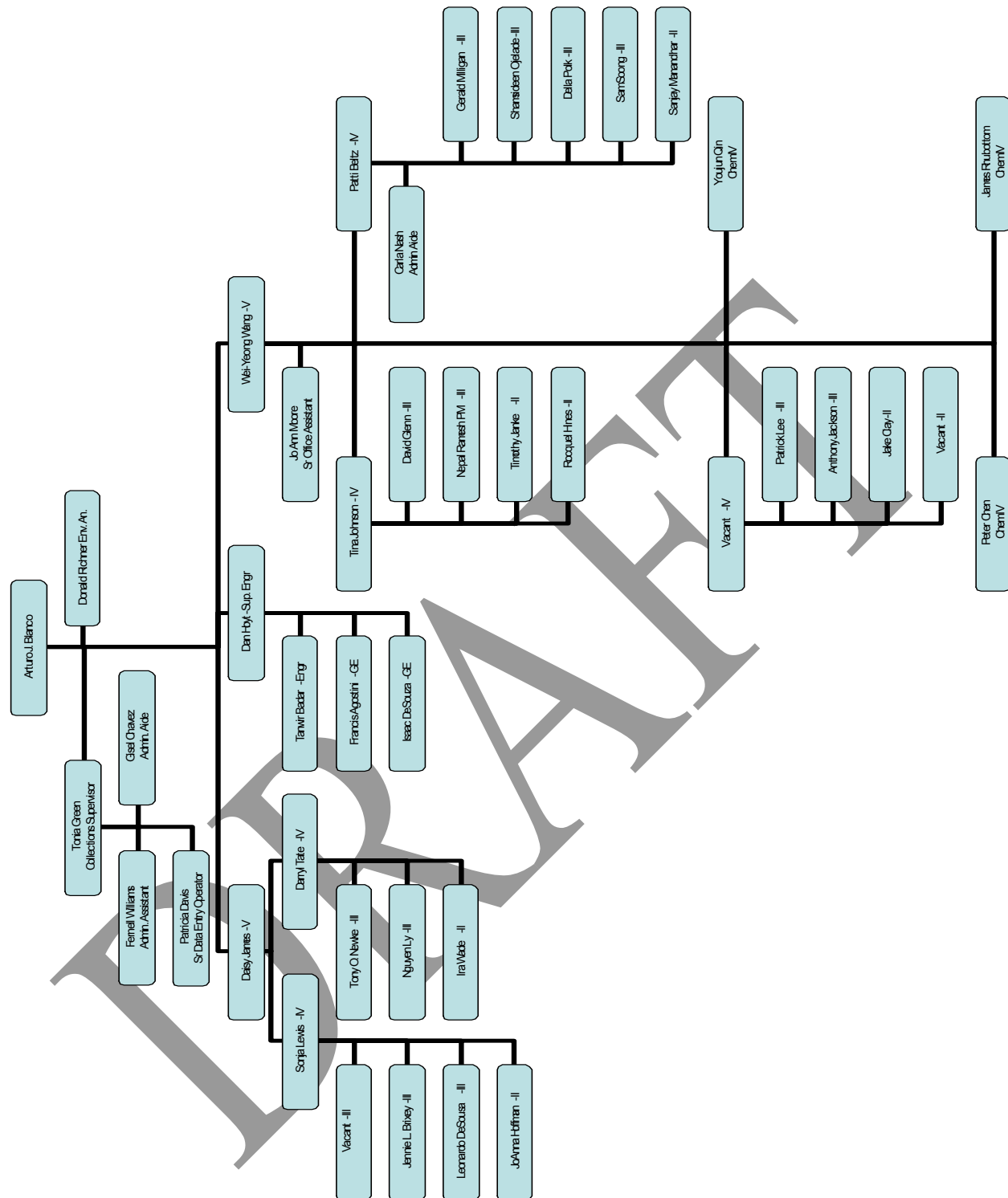


Figure 2: BPCP organization chart

Houston Department of Health and Human Services Bureau of Pollution Control and Prevention Mobile Laboratory Program Team

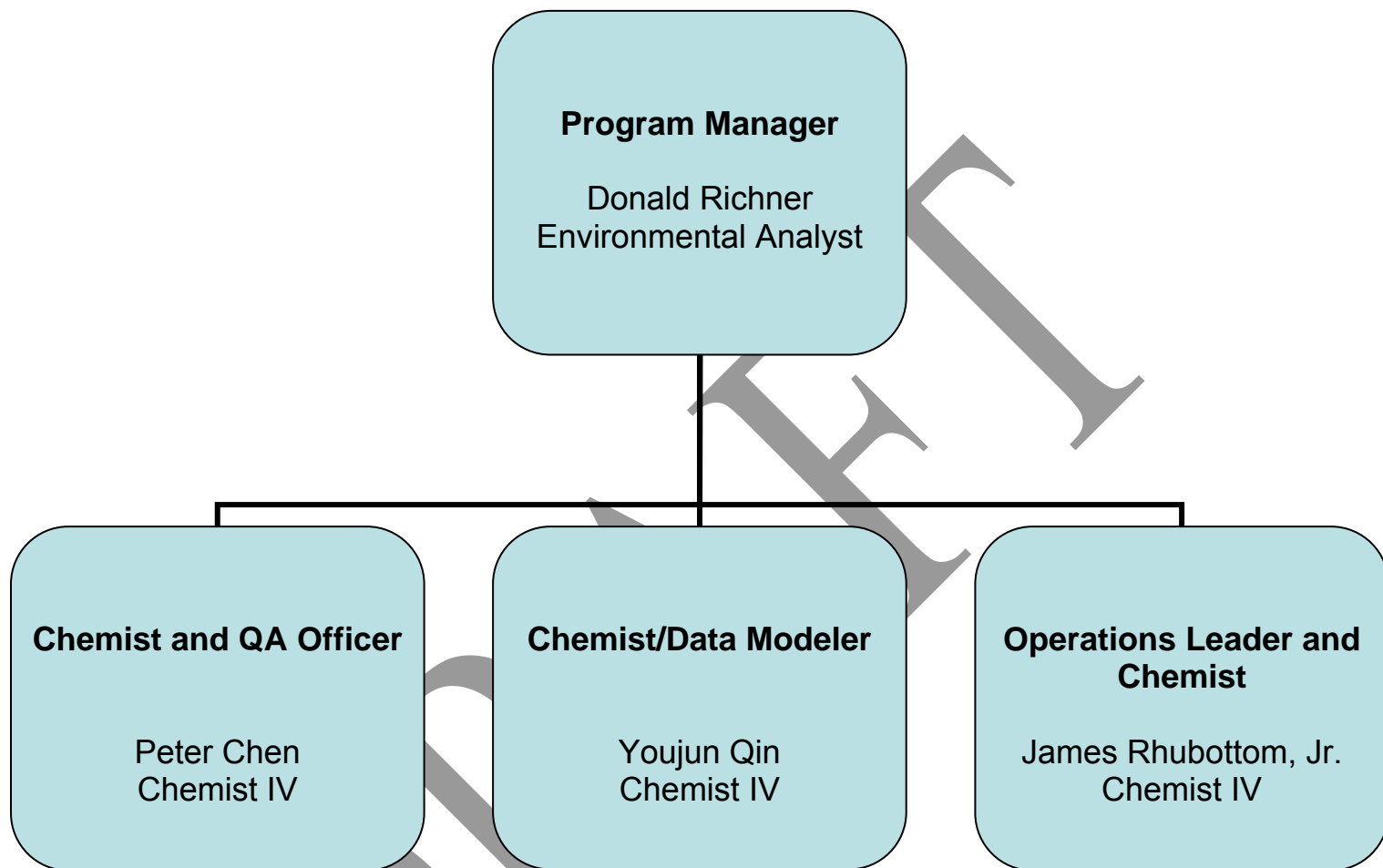


Figure 3: MLP organizational chart

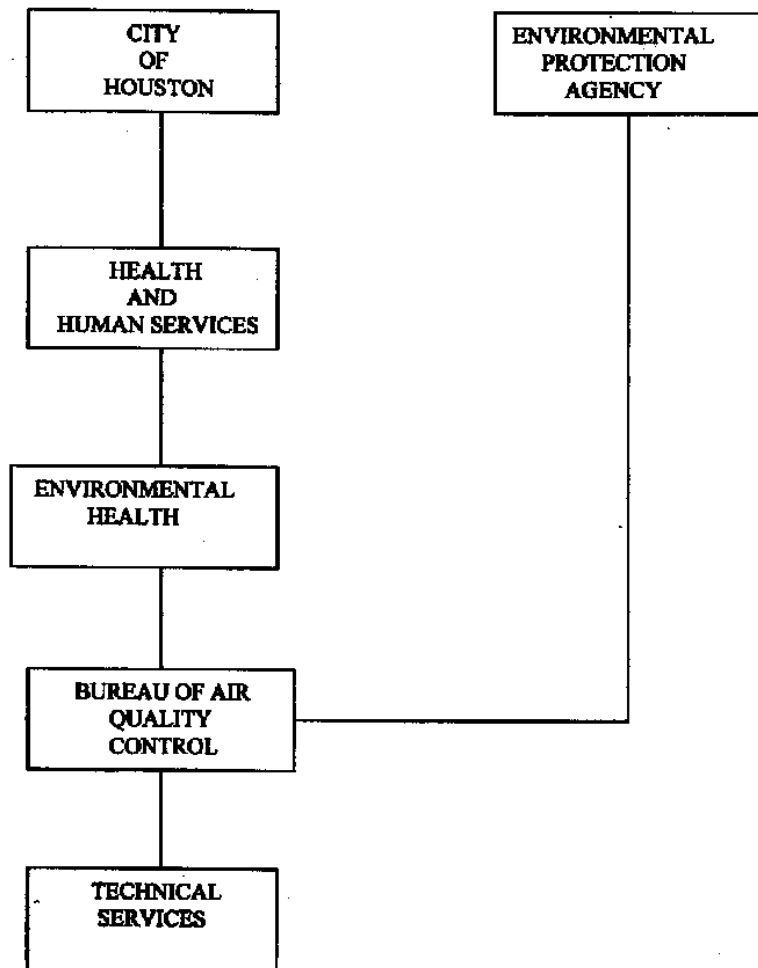


Figure 4: MLP Regulatory Relationship

A5. Problem Definition/Background

Houston has extremely difficult air toxics challenges to address due to the significant impact of air emissions from one of the largest petrochemical complexes in the world. The citizens of Harris County, home to Houston, faced exposure to over 19 million pounds of hazardous air pollutants in 2003, including 456,333 pounds of 1,3-butadiene and 750,325 pounds of benzene according to the EPA's 2003 Toxic Release Inventory (TRI) report. The Texas Air Quality Study in 2000, a study that involved over 200 scientists and more than \$20 million, used aircraft to measure volatile organic compounds (VOCs) above refineries and chemical plants in the Houston area. The study found VOCs concentrations approximately 6 times higher than VOC emissions reported by the petrochemical facilities. Since TRI data uses many of the same estimating techniques used in reporting VOC emissions, the underreporting of air toxic emissions seems very likely as well. Harris County remains particularly vulnerable to air toxics exposures since the production and supplying of a significant portion of the nation's benzene, 1,3-butadiene, and other hazardous air pollutants originate from some of the HSC area petrochemical facilities.

The method that DHHS has utilized for measuring air toxics involved the collection of a SUMMA® canister sample at a given location and delivery to an offsite laboratory for analysis. However, the instability of many chemicals, such as 1,3-butadiene, resulted in sample degradation long before sample introduction into the analyzer. As a result this neither accurately accounted for ambient air concentrations of 1,3-butadiene nor eased the concerns of citizens in the HSC area who stood to face the brunt of any air toxics exposures from nearby industries.

The Houston area has more air monitoring stations than any major city in the United States, with 45 different locations measuring ozone and other air pollutants and eight fixed auto-gas chromatograph (auto-GC) stations in the HSC area that can measure parts per billion carbon (ppbC) levels of over 45 different volatile organic compounds (VOCs) in the ambient air. However, these monitoring stations focus primarily on ozone concentrations directly or on relatively high concentrations of ozone precursors. The existing monitoring stations have no capability to provide accurate measurements of low concentrations of air toxics. Additionally, the area has an insufficient number of available fixed monitors to perform source identification and/or source characterization.

The HDHHS has become a national leader in applying proven best-in-class mobile laboratory monitoring technologies towards developing processes for source identification and characterization of air toxics. The MLP team uses MAAML data to assess the ambient air quality, identify VOCs source emissions, estimate source contributions, evaluate air quality models, and develop air pollution control strategies and implementation plans. The data also supports permitting, policy creation, community exposure monitoring, and enforcement activities within BPCP.

A6. Project/Task Description

Many of the HSC industries share a common fence line and neighboring companies frequently use or produce similar chemical compounds. The close proximity of multiple petrochemical plants makes it extremely difficult to identify the source of emissions. The instruments in the mobile laboratory measure many different compounds in addition to air toxics of interest such as 1,3-butadiene and benzene. By placing the mobile laboratory at several surrounding locations and measuring wind direction and speed, the monitoring data characterize a range of emissions to "fingerprint" or identify the emission patterns of specific facilities.

The initial program target, the Milby Park area in Houston, provided an excellent case study, as two nearby companies, Goodyear and Texas Petrochemicals (TPC), share a common boundary and incorporate 1,3-butadiene in their production processes. These two plants also lie within one mile of Cesar Chavez High School (CCHS) and the auto-GC located there. The EPA has classified 1,3-Butadiene as one of 188 hazardous air pollutants of greatest concern due to its potential contribution to population risk. According to the EPA Integrated Risk Information System (IRIS), the carcinogenic risk from chronic inhalation exposure for 1,3-butadiene stands at 1 in 100,000 for a concentration of $0.3 \mu\text{g m}^{-3}$. Meanwhile, the auto-GC in Milby Park recorded annual average concentrations of 1,3-Butadiene of 1.54 ppbV ($\approx 3.52 \mu\text{g m}^{-3}$ at 288 °K, 101,350 Pa) and 1.13 ppbV ($\approx 2.58 \mu\text{g m}^{-3}$) for 2005 and 2006, respectively. These readings represent 11.8 and 8.6 times, respectively, the 1 in 100,000 carcinogenic risk level listed in IRIS.

Point source characterization comprises a critical element of the MLP in order to identify specific point source emissions. Each facility used different production processes; thus, the "fingerprint" or emissions pattern of chemicals released into the air by any single facility will differ from the other nearby facilities. Data obtained from the MAAML combined with speciated VOC concentrations measured by all relevant auto-GCs creates the "fingerprints" for Goodyear and TPC to identify which facility caused which emissions events as well as which units within each facility generated the highest emissions.

Upon study completion, HDHHS has applied the same technology and approach, with modifications based on experience from the Milby Park project, to monitor those areas of Houston showing elevated levels of air toxics, such as Allendale and Manchester among others. HDHHS continues to collaborate with the EPA to identify the best means for sharing the experience with other local, state, and national government agencies for continuous improvement of their own techniques as well as providing guidance to help others resolve their issues with source identification.

A7. Quality Objectives and Criteria

The MAAML includes a gas chromatograph with flame-ionization and mass spectrometric detectors (GC/FID/MSD) system. The analytical methods for speciated VOCs concentrations derive from EPA Compendium Methods TO-14A, "Determination of Volatile Organic Compounds (VOCs) in Ambient Air Using Specially Prepared Canisters with Subsequent Analysis by Gas Chromatography" and TO-15, "Determination of Volatile Organic Compounds (VOCs) in Air Collected in Specially-Prepared Canisters and Analyzed by Gas Chromatography/Mass Spectrometry". The MLP team also incorporates EPA Technical Assistance Document for Sampling and Analysis of Ozone Precursors into the MAAML analytical methods. For monitoring runs, the MAAML uses near real-time continuous sampling procedures instead of canister sampling methods for sample acquisition. In addition, the GC has dual columns with an FID and an MSD. For purposes of this document, the MLP team defines VOCs as organic compounds having a vapor pressure greater than 10^{-1} torr at 25°C and 760 mm Hg. Table 1 lists possible target compounds of VOCs. Table 2 lists airborne pollutants emitted from two target facilities, Goodyear and TPC.

Detection Limits

The detection limit indicates the lowest theoretical concentration at which an analytical instrument can distinguish a particular compound with 99% confidence level. The detection limit of an instrument usually varies slightly due to instrument quality and the statistical methods involved in establishing instrument detection limits. The method detection limit (MDL) typically denotes a detection limit generated by instrumentation trials.

The MDL goal for the FID stands at ≤ 0.5 ppbV-C for most targeted compounds.

The MDL goal for the MSD stands at ≤ 0.2 ppbV for most targeted compounds.

Precision

Precision designates the measurement of the repeatability of a measurement. The MLP team will conduct all instrument precision checks in accordance with 40 CFR, Part 58, Appendix A. The 95% probability limits for all instruments must fall within $\pm 25\%$. The replicate precision specifies the absolute value of the difference between replicate measurements of the quality control or field sample divided by the average value with final expression as a percentage.

Accuracy

Accuracy reflects the degree to which measured values match true or accepted values. The MLP team will conduct all instrument accuracy checks in accordance with 40 CFR, Part 58, Appendix A. The 95% probability limits for all instruments must fall within $\pm 30\%$ recovery. The accuracy reflects the difference between the nominal concentration of the audit compound and the measured recovery divided by the concentration of the audit compound with final expression as a percentage.

Completeness

The MLP team will target data capture at 75% of the total number of possible samples for each MAAML sampling trip under normal operating conditions.

Table 1: Target VOCs

Name	CAS No.	MDL (ppbv)	Name	CAS No.	MDL (ppbv)
ethane	74-84-0	0.1	Benzene	71-43-2	0.2
ethylene	74-85-1	0.1	Carbon Tetrachloride	56-23-5	0.8
propane	74-98-6	0.1	1,2-Dichloropropane	78-87-5	0.5
Dichlorodifluoromethane	75-71-8	0.8	Trichloroethylene	79-01-6	0.2
propylene	115-07-1	0.1	Cis-1,3-dichloropropene	10061-01-5	0.4
acetylene	74-86-2	0.1	Trans-1,3-Dichloropropene	10061-02-6	0.2
Methyl chloride	74-87-3	0.3	1,1,2-Trichloroethane	79-00-5	0.3
1,2-Dichlorotetrafluoro...	76-14-2	0.4	Toluene	108-88-3	0.2
Vinyl chloride	75-01-4	0.2	1,2-Dibromoethane	106-93-4	0.2
1,3-Butadiene	106-99-0	0.4	Tetrachloroethylene	127-18-4	0.3
n-Butane	106-97-8	0.2	1,1,1,2-tetrachloroethane	630-20-6	0.2
Bromomethane	74-83-9	0.2	Chlorobenzene	108-90-7	0.1
Ethyl Chloride	75-00-3	0.3	Ethylbenzene	100-41-4	0.1
Trichlorofluoromethane	75-69-4	0.1	m/p-xylene	108-38-3 & 106-42-3	0.3
n-Pentane	109-66-0	0.1	Styrene	100-42-5	0.1
1,1-Dichloroethylene	75-35-4	0.1	o-Xylene	95-47-6	0.1
Methylene Chloride	75-09-2	0.3	1,1,2,2-Tetrachloroethane	79-34-5	0.3
1,1,2-Trichlorotrifluoro...	76-13-1	0.3	Cumene	98-82-8	0.2
1,1-Dichloroethane	75-34-3	0.2	1,3,5-Trimethylbenzene	108-67-8	0.1
2-methylpentane	107-83-5	0.1	1,2,4-Trimethylbenzene	95-63-6	0.1
1-Hexene	592-41-6	0.1	1,3-Dichlorobenzene	541-73-1	0.1
Cis-1,2-Dichloroethylene	156-59-2	0.3	1,4-Dichlorobenzene	106-46-7	0.1
Hexane	110-54-3	0.1	1,2-Dichlorobenzene	95-50-1	0.2
Chloroform	67-66-3	0.5	1,2,4-Trichlorobenzene	120-82-1	0.4
1,2-Dichloroethane	107-06-2	0.4	Hexachloro-1,3-Butadiene	87-68-3	0.3
1,1,1-Trichloroethane	71-55-6	0.6			

Table 2: Air pollutants emitted from Goodyear and TPC

Goodyear		TPC	
Styrene	PM10	1,3- butadiene	PM10
1,3- butadiene	PM2.5	Butene	PM2.5
Trimethylbenzene	VOC (Unclassified)	Isobutane	VOC (Unclassified)
Ethylbenzene	NO _x	n-Butane	NO _x
Toluene	SO ₂	Pentane	SO ₂
Xylene	CO	Ethylene	CO
Octane	Formaldehyde	Propylene	Methyl tert-butyl ether
Cyclohexane	Acetaldehyde	Isobutene	Olefins
Propane	Acrolein	Ethane	Fuel Oil
Butene	VOC Gas Mixture	Propane	Methanol
<i>cis</i> -2-butene	Talc	Isobutylene	Furfural
Isobutene	Ketones		Diisobutylene
<i>trans</i> -2-butene	Olefins		Dimethylformamide
	Vinyl Cyclohexene		Methane
	Paraffins (Cyclic)		Naptha
	Carbon Disulfide		Gasoline
	Gasoline		
	Mercaptans		
	Ammonia		
	Peroxides		
	Diesel		
	Kerosene		
	Sulfuric Acid		
	Mineral Spirits		
	Chlorine		

A8. Special Training/Certification

All technical personnel hired for the MLP have college degrees in either an engineering discipline or a scientific discipline. In addition, all members of the MLP team have experience in operating GC/FID/MS systems. All team members will also attend training provided by the MLP contractors to include hands-on training with the MLP equipment and related analytical instruments.

The MLP team compiles the Standard Operating Procedures (SOPs) and updates them based upon field monitoring experience. The MLP team must also receive training in field sampling, defensive driving, first aid, and emergency procedures.

A9. Documentation and Records

The MLP team must document and maintain accurate records for all mobile laboratory activities. These records include site information, instrument operation, maintenance, calibrations, sample collection, analysis, data review, and data reporting. This allows the opportunity for historical reconstruction of all activities contributing to the creation of the final report detailing MLP accomplishments.

The documents maintained include the QAPP, methods, sampling plans, SOPs, and logbooks. All documentation must have a document title, a control number, a revision number, supervisor and QA approval signatures, and an effective date. The hard copy documents with the original signature represent the official copies of these documents. Each document will remain in effect until superseded by a later version or until the completion of the project for which they apply while maintaining expired versions in a secure file for a minimum of five years beyond their expiration date.

Upon the filling of all logbooks containing data, sample, or analysis information, MLP personnel will store them at 7411 Park Place, Houston TX until the filling of the next logbook. Thereafter, MLP personnel will send filled logbooks to the City of Houston, DHHS storage facilities for five years with subsequent destruction.

As required by regulations or project guidelines or for five years, as determined by the greater length, the MLP team will store analytical data records such as, but not necessarily only, the following:

- Chain-of-custody records
- Sample collection records
- Sample control records
- Sample and standard preparation records
- Analytical records
- Analytical data and results records
- Records of maintenance activities
- Records of audit activities
- Analytical standards and certifications

The MLP team will immediately record all activities associated with sample and standard preparation records such as, but not necessarily only, the following:

- Sample identification
- Sample preparation (cleanup, extraction, digestion, pressurization, sample spiking, etc.)
- Standard and reagent origin, receipt, preparation and use
- Any observation and/or deviations from SOPs
- Date and analyst initials

Analytical logs will hold information on sample analysis. The information includes the following:

- Instrument operation conditions and methods
- A chronological list of all analyses on the instrument including sample and standard identification numbers
- Injection volumes and dates
- Sample dilutions or spikes
- Calculations
- Electronic file information for each sample
- Comments
- Analyst initials

Analytical data consists of all records produced during sample analysis such as instrument printouts and chromatograms. MLP personnel will save raw data records produced by the instrument in an electronic format and/or as a hard copy with finalized results and raw data stored on electronic media periodically.

B. DATA GENERATION AND ACQUISITION

B1. Sampling Process Design

The MLP team designed the MAAML to monitor ambient air toxics *in situ* with species concentrations of VOCs determined immediately after collection. The MAAML includes equipment to document geographic location along with measurement of meteorological parameters such as wind speed, wind direction, ambient temperature, humidity, and atmospheric pressure.

The initial targets of the project, Goodyear and TPC, shared a common boundary and incorporate 1,3-butadiene in their production processes. A major task of the project centered on identifying which facility caused the majority of 1,3-butadiene emissions and which part of which facility produced these emissions.

MLP Chemists found a viable MAAML deployment site along the eastern fenceline of TPC that separated TPC from Goodyear. Based on emission inventories of TPC and Goodyear and meteorological data measured at Milby Park, MLP Chemists used the ISC3 model to simulate 1,3-butadiene concentration distribution around the two facilities to identify suitable positions for MAAML monitoring. By appropriately positioning the MAAML and comparing speciated VOC concentrations measured at this site to those measured by the auto-GCs at Milby Park and CCHS, MLP Chemists accomplished MLP source characterization and identification objectives.

B2. Sampling Method

The MAAML analytical platform starts with a pre-concentrator/Thermal Desorber (TD) combined with an air server composed of a mass flow controller (MFC) and a pump to draw ambient air samples at a specified rate into the instrumentation. A Nafion dryer removes excess moisture in the ambient sample. A multitrap cryogenic concentrator concentrates the sample to achieve high analytical sensitivity for very low concentrations of air toxics. After collection of a desired amount of sample, the TD rapidly heats the trap to desorb the sample and inject it into the GC. The following summarizes the sampling procedures:

Sampling method:	Near real-time continuous GC/FID/MS sampling
Collection media:	Multitrap cryogenic concentrator, Markes Air Server and UNITYe TD, or equivalents
Instrumentation:	Agilent 6890N GC w/dual columns, heated Deans switch, and FID; Agilent 5975 Inert Turbo MSD, or equivalents
Sample flow rate:	15 mL min ⁻¹
Sample collection period:	40 min
Sample volume:	600 mL
GPS:	GPS16-HVS or equivalent
Meteorological:	MetOne 50.5 Sonic Wind Sensor, Met One 060A Temperature Sensor, Met One 083D Relative Humidity Sensor, Met One 092 Barometric Sensor; or equivalents

B3. Sample Handling and Custody

MLP Chemists do not directly handle discrete samples for the MLP. MLP Chemists electronically document the identity and disposition of samples by using a run log established with the GC/FID/MS support computer and processing software. A datalogger records the analog meteorological data and then converts the data to digital for processing by the support computers and software. The processing software maintains an audit trail of all data transfers and processing activities associated with electronic data files, and with hardcopies maintained in site-specific binders. All electronic data files and data measured by meteorological instruments have the option of transferral to the Active and Intelligent Monitoring (AIM) server via wireless modem for secure storage. The AIM server can provide real-time web-based access for analyzing results.

B4. Analytical Method

The MLP team will perform the primary sample analyses based upon EPA Compendium Method TO-14A, "Determination of Volatile Organic Compounds (VOCs) in Ambient Air Using Specially Prepared Canisters with Subsequent Analysis by Gas Chromatography" and Method TO-15, "Determination of Volatile Organic Compounds (VOCs) in Air Collected in Specially-Prepared Canisters and Analyzed by Gas Chromatography/Mass Spectrometry". The MLP team also refer to the EPA Technical Assistance Document for Sampling and Analysis of Ozone Precursors. Procedural modifications include the incorporation of MS instrumentation and use of near real-time continuous sampling procedures rather than the lack of MS instrumentation and use of canister sampling methods described in EPA Methods TO-14A and TO-15.

The GC has dual capillary columns that couple to an FID and an MSD. MLP Chemists use the MSD to examine mass spectra for individual peaks in the total ion chromatogram with respect to the fragmentation pattern of ions corresponding to various VOCs, including the intensity of primary and secondary ions. Comparing the fragmentation pattern with the National Institute of Standards and Technology (NIST) traceable reference spectra allows the MLP Chemists to identify the compound. For any given compound, the MSD compares the intensity of the quantitation ion with the system response to the fragment for known amounts of the compound. This establishes the compound concentration in the sample.

MLP Chemists use the FID for the quantitation of light species such as ethane, ethylene, and acetylene with the identification of these compounds based on matching retention times and peak patterns of standards containing known analytes.

B5. Quality Control

The Quality Control (QC) protocol for the MLP includes the following:

- Sampling system contributions to the final measurements
- Analytical system contributions to the final measurements
- Qualitative performance of the method
- Quantitative performance of the method
- Precision of the measurements
- Accuracy (bias) of the measurements

QC activities for meteorological equipment include visual inspection of instrumentation integrity, measurement consistency with current conditions, and corrective actions while QC activities for GPS equipment will reflect manufacturer's guidelines.

Tables 3 and 4 list the QC activities for the MS and overall GC/FID/MS system.

Table 3: QC Activity – MS: Required BFB Key Ions and Ion Abundance Criteria

Mass	Ion Abundance Criteria
50	8.0 to 40% of mass 95
75	30 to 66% of mass 95
95	Base peak, 100% relative abundance
96	5.0 to 9.0% of mass 95
173	<2% of mass 174
174	50 to 120% of mass 95
175	4.0 to 9.0% of mass 174
176	93 to 101% of mass 174
177	5.0 to 9.0% of mass 176

¹All ion abundances must be normalized to m/z 95, the nominal base peak, even though the ion abundance of m/z 174 may be up to 120 percent that of m/z 95; based on EPA Compendium Method TO-15.

Table 4: GC/FID/MS QC Activities - General

QC Check	QC Procedure	Frequency	Acceptance Criteria	Corrective Action
MDL study	Follow 40 CFR Part 136 App.B	Annually or after major system or procedural modification	FID: <0.5 ppbV-C for most target compounds. MS: <0.2 ppbV for most target compounds.	1) Rerun MDL study. 2) If fails again, perform instrument maintenance to increase sensitivity.
PFTBA - MS tune and check for leaks	Autotune	Prior to analyzing samples	1) Must pass BFB acceptance criteria. 2) Mass/Energy % relative abundance 69-100 28-<30% 18-<10%	If leak is apparent, fix leak to meet criteria
BFB Tune check	Trap 50 ng BFB under the optimized preconcentration	Prior to analyzing samples	See Table 3	Retune instrument and if necessary clean source
Internal Standard	Multiple component injected with each sample	Every ambient and QC sample	50%-150% recovery compared to the passing QC sample	Determine problem and/or flag results
Calibration (linearity)	FID: Five concentrations plus a method blank MS: Five concentrations plus a method blank	Annually, or after major system or procedural modifications, or CVS or LCS routinely fails	FID: Calibration curve correlation coefficient (r) ≥ 0.995 or RSD of RFs <20% MS: Calibration curve correlation coefficient (r) ≥ 0.995 or RSD of RFs <30%, with two exceptions of <40%.	1) Identify and repeat analysis of outlying points; recalculated using repeated points. 2) If out, identify and correct problem, then rerun
Calibration Verification Standard (CVS) – recovery and analytical drift	Mid-level standard	Daily	70%-130% recovery compared to the curve for all target compounds	1) If more than 10% of the target compounds fail, reanalyze 2) If fail, perform corrective action
Method Blank - system contribution to measurement	Humidified UHP air sampled under normal conditions	Daily	FID: 1) Target compound concentrations ≤ 2.0 ppbV-C 2) TNMHC values ≤ 20.0 ppvV-C MS: Target compound concentrations ≤ 0.5 ppbV	1) Improve system performance to meet spec. and invalidate those target compounds back to the last acceptable blank and until an acceptable blank is performed 2) Improve system performance to meet spec. and invalidate the TNMHC values back to the last acceptable blank and until an acceptable blank is performed
Calibration Verification Standard Duplicate (CVSD) – precision	Mid-level standard	Weekly	Precision: $\leq 25\%$ RPD for most compounds	Perform system maintenance, recalibrate, or qualify affected results as appropriate

MLP Chemists set up and operate all ambient air monitoring instruments according to manufacturer's recommended specifications with initial verification using standard calibration procedures. MLP Chemists must demonstrate that all instruments operate within manufacturer's specifications before deploying on field sampling runs.

When appropriate, the laboratory will evaluate repaired instruments, data acquisition equipment, software, and system upgrades. If the instruments fail to meet specifications and MLP Chemists cannot make the necessary corrections, they will notify the QA Officer and Program Manager as well as the instrument manufacturer. The manufacturer will correct the instruments under warranty with non-repairable instruments returned to the manufacturer. If the manufacturer only needs to send repair parts, the MLP Chemists will complete the repairs and perform the relevant instrumentation checks. MLP Chemists will use only NIST traceable standards for reference materials for calibrations and other instrument checks.

MLP Chemists practice routine preventive maintenance based upon manufacturer's recommendations to minimize instrument downtime. Routine preventive maintenance includes replacing the sample lines, cleaning the FID reaction chamber, cleaning the ion source, replacing filaments, and column conditioning as needed. Additionally, routine preventive maintenance data includes verifying that the values recorded from the meteorological and GPS equipment correspond to current atmospheric and geographic conditions. Finally, MLP Chemists note any discrepancies in the maintenance logbooks.

B7. Instrument Calibration and Frequency

Before sample analysis, analysis of calibration standards containing each target analyte establish GC/FID/MS response, linearity, and sensitivity. MLP Chemists perform instrument calibration using calibration standards spanning the expected sample concentrations. The instrumentation calculates analyte concentrations using multipoint calibration response factors while the MLP Chemists confirm calibration accuracy using second source standards when available. MLP Chemists will purchase only NIST traceable standards from commercial vendors.

MLP Chemists perform initial calibrations upon: (1) instrument evaluation prior to analyzing samples; (2) addition of analytes to the analysis; or (3) instrument response drift such that the calibration verification sample does not meet established acceptance criteria.

For the FID, the MLP team will prepare calibration curves by analyzing five calibration standard concentrations and a blank. For the MSD, the MLP team will prepare calibration curves by analyzing five calibration standard concentrations and a blank. The lowest concentration should lie near but slightly above the MDL and the highest concentration should exceed the highest expected sample concentration to the upper limit of instrument's linear range. Ending with analysis of a blank allows for the assessment of system carry-over.

A calibration verification standard (CVS) provides for daily calibration verification through comparing the concentration recoveries of the CVS with the acceptance criteria. If the results fall outside the accuracy objectives, the MLP Chemists determine the assignable cause, document it, and corrected before continuing a sample analytical run, flagging the data where appropriate.

At least annually, the MLP Chemists will conduct qualitative and quantitative performance checks on the GPS equipment and meteorological sensors according to all relevant manufacturer's guidelines. MLP Chemists will document the performance checks and their results as well as any repairs affected in the appropriate logbooks. MLP Chemists will also communicate this information to both the Program Manager and QA Officer in a timely manner in order to ensure proper operation of the GPS and meteorological equipment per reporting requirements.

B8. Inspection/Acceptance of Supplies and Consumables

The MLP team purchases all items to support the MLP (including high purity helium cylinders, DI water for H₂ generator, GC columns, cold traps, meteorological sensor calibration kits, etc.) while purchasing consumables directly from the instrument manufacturers. When unavoidable, the MLP team will acquire consumables from another reputable manufacturer in accordance with all City of Houston, HDHHS purchasing guidelines. The MLP team specifies all supplies and consumable for acceptable quality and checks for that quality upon receipt. If the item does not meet the specifications, the MLP team contacts the supplier to correct the item or replace it.

The MLP team will purchase gaseous standards for Calibration Verification Standard (CVS) and Retention Time Standard (RTS) from commercial suppliers who provide standards NIST traceable. The suppliers must also tag the standards with an expiration date with all replacement standards purchased and certified prior to standard expiration. The MLP team may also send the expired standards back to the manufacturer for recertification.

B9. Non-direct Measurements

The MLP will use atmospheric dispersion models to assess the impact of source emissions on ambient air quality. With significant experience in various modeling protocols, MLP Chemist Dr. Youjun Qin will lead the MLP team in the application of the various models on MLP collected data. Using emission inventories of Goodyear and TPC, MLP personnel will use atmospheric dispersion modeling (ISC3) to simulate 1,3-butadiene annual and monthly average concentration distributions around Goodyear and TPC in 2006 to find some suitable locations for mobile monitoring. MLP staff will also apply ISC3 modeling to predict the hourly average 1,3-butadiene concentrations for MLP monitoring periods and then evaluate the ISC3 model results as compared with actual 1,3-butadiene concentrations as measured by the MAAML and auto GCs at Milby Park and Cesar Chavez. Through analysis of the atmospheric dispersion model results, MLP personnel can identify the major contributors for ambient 1,3-butadiene.

Environmental scientists have developed several receptor models to identify airborne pollutant emission sources and estimate source contributions in ambient air pollution; however, the reliability of atmospheric dispersion models depends upon emission inventories. There might be some potential emission sources that were not listed in the emission inventories. To identify these potential sources and estimate the source contributions, the Program team applied Positive Matrix Factorization (PMF) modeling to analyze the VOC species data measured by the MAAML and by the auto-GCs at Milby Park and Cesar Chavez in order to identify the major VOC emission sources and source contributions. By comparing results from dispersion and receptor modeling, the MLP team looked to derive the most precise and reliable results allowed by the collected data.

Back trajectory creation or event reconstruction can aid in identifying source direction. The MLP team will employ the University of Houston's Real-Time Interactive Trajectory System (RITS) (<http://server2-aqm.geosc.uh.edu/RITSweb>) to simulate back trajectories upon MAAML detection of high 1,3-butadiene concentrations in order to trace the emissions back to their source. Additionally, the Program team applied the RITS to identify major 1,3-butadiene emission points in Goodyear and TPC. In addition, MLP Chemists constructed the potential source contribution function (PSCF) to describe quantitatively potential source distributions. Lastly, the Program team attempted to identify some potential sources not listed in the inventories by comparing and analyzing the results of atmospheric dispersion models, receptor models, and backward trajectory models.

B10. Data Management

GC/FID/MS analytical data storage occurs via PC-based data acquisition software (EnviroQuant ChemStation® from Agilent Technologies) with the data transferred to Excel spreadsheets for calculation, comparison, and reporting purposes.

A datalogger converts the analog data collected from the GPS and meteorological equipment to digital and then downloads all the data to a PC-based program used for data summarization, validation, and reporting. The MAAML onboard computer stores the GPS, GC/FID/MS, and meteorological data upon collection. The MLP team archives the stored data to an appropriate medium (typically compact discs) for data preservation on a weekly basis. Archiving will occur for all other MLP data, including sampling notes, pictures, summary reports, and all other project specific information with a frequency appropriate to the medium used for data collection. To prevent data loss from electrical power interruptions during an analytical run, the MAAML will have two generators in operation. As either generator alone has the capacity to power all MAAML analytical instrumentation, failure of one generator will not result in data loss during a sampling event. A support vehicle will allow MLP Chemists to ability to replenish generator fuel supplies at any point during a run as a further means of preventing data loss.

A wireless modem transmits the GC/FID/MS, GPS, and meteorological data to the AIM server for secure offsite storage. The AIM server also provides a web-based access to monitor and analyze the results. The contractor providing the AIM software will retain responsibility for operation and maintenance of the offsite server to include daily backup of all stored MLP data in the AIM database. Upon discovering any problems with the offsite server, especially concerning data loss, the contractor will contact the Program Manager immediately. Since MLP Chemists will retain copies of all raw MLP data as stated above, avoidance of permanent data loss resulting from server failure will occur via the uploading of data from either the MAAML TD/GC/FID/MSD PC workstation or another MLP PC to replace the data lost from the offsite server database. The MLP Program Manager, with input from the QA Officer, oversees and retains final responsibility for the safety and security of all stored data, both onsite and offsite. With the aforementioned measures in place, MLP personnel anticipate a data capture efficiency of no less than 75% while continually seeking ways to achieve a higher percentage.

C. ASSESSMENT AND OVERSIGHT

C1. Assessment and Response Actions

The QA Officer, with input from the MLP team, reviews and audits the QA/QC program for the MLP on an annual basis and certifies that the QAPP accurately reflects any MLP procedural updates or modifications. After performance of the annual review, the QA Officer details any necessary updates or modifications to the QAPP and delegates an MLP staff member to revise the QAPP. Upon receipt of the revised QAPP, the QA Officer reviews it to ensure the accuracy of all changes and submits it to the Program Manager for review and submission to the EPA Region 6 Project Officer for review and approval. This review, along with other reviews and audits, ensures that the data-generating, data-gathering, and measurement activities produce reliable and accurate results. Individual audit reports specify required response, method response, and response deadlines. If a finding requires a response and said response does not return within the designated time, or if dispute arises from the proposed corrective action without a timely resolution, the QA Officer will engage successively higher management levels regarding the recommendation and/or conflict to achieve an acceptable resolution. The QA Officer and Program Manager also will suspend all field sampling events until implementation of all CARs demonstrates a satisfactory resolution of the non-conformance. If the QA Officer identifies a non-conformance during any review or audit, then s/he immediately discusses the findings with the MLP Chemists for clarification and generation of a corrective action report (CAR) as necessary. The QA Officer submits the final report including relevant CARs to the Project Manager for review.

MLP personnel use data quality reviews to assess the accuracy, completeness and limitations of a data set by examining data recording and data transfer. MLP Chemists peer-review all data to include quality control spreadsheets, daily quality control samples, and method blanks at least once per mobile laboratory trip. The Program Manager and QA Officer perform spot checks on all logbooks, instrument sequences, and standard validation sequences at least monthly. The QA Officer immediately reviews any potential QA issues with the MLP Chemists. The Chemists then correct and flag any impacted data as necessary with the QA Officer reviewing all changes prior to final approval.

The Program Manager and QA Officer review all sampling techniques at least quarterly. MLP Chemists check the sampling trains for flow rate and volume accuracy using a calibrated rotameter and record any necessary adjustments in the maintenance logbook. As deemed necessary by Program Management, a cleaned and blanked canister will collect a co-located field sample directly next to the MAAML input port at a similar sampling rate. MLP Chemists will ship the canister to a NELAC-certified laboratory for ambient air analysis of all analytes of interest, including TICs, by an approved air toxics method (ex. TO-15, TO-14A). The QA Officer receives findings from the outside laboratory for comparison to the MAAML's findings of the co-located sample, comparing each laboratory's results for qualitative findings, analyte concentrations, and possible systematic contaminations. As necessary, the QA Officer discusses and reviews any discrepancies between the field and audit samples with the Chemists. If required, MLP Chemists check the MAAML system for systematic or instrumentation problems and correct them, recording any necessary adjustments necessary in the maintenance logbook.

The QA Officer conducts technical system and performance audits once per calendar year per Chemist with performance and data evaluations closely monitored as well. This QAPP sets the definition of a technical systems audit as a thorough and systematic qualitative review. It

represents an assessment of the overall implementation of and compliance with the laboratory guidance documents. It further denotes an objective evaluation of the analytical system as a whole with respect to strength, deficiencies, and potential areas of concern. MLP technical systems audits will include the following:

- Personnel and training
- Facilities and equipment
- Procedures and documentation
- QC procedures and documentation
- Logbook procedures
- Data review and validation procedures
- Data reporting procedures
- Data archival and record keeping procedures

The performance audits utilize NIST traceable-secondary source standards prepared by staff from a different organizational unit (EPA or TCEQ) and submitted as blind samples to the laboratory. MLP Chemists report all measured results, theoretical values, and calculated recoveries to the QA Officer who compares the analyte concentrations to the theoretical standard concentrations. The QA Officer will accept any analyte concentration results within $\pm 50\%$ recovery of the theoretical value as passing. If any analytes fall outside of this criterion, then the Chemist who performed the analysis containing the outlying data must reanalyze the audit sample. If any analyte continues to fail criteria, the QA Officer implements a full system review to discover any systematic or instrumentation errors with any changes performed to the analytical system reported and reviewed by the Program Manager and QA Officer. MLP Chemists record any adjustments necessary in the maintenance logbook. The QA Officer stores all audit results in a database for trend analyses and for later reference in determining sample constituents and concentrations for future audits. Each analyst must perform the demonstration of capability (DOC) of the audit sample with passing criteria, from login to final reporting, before receiving approval to perform any field sampling.

The QA Officer reviews all calculations used during the creation of the final report before final report distribution. Only MLP Chemists, the QA Officer, the Program Manager, and the AIM database IT technicians will have access to the final database. An automated audit trail in the data reviewing software, traceable to individual passwords and workstations, records all access to the database especially any manual changes to the data, including sample information or manual integrations. A wireless modem transmits the raw data generated by the instruments to the AIM database. Quarterly, the QA Officer verifies that the raw data matches the transmitted data. All data generated undergoes peer-reviewed by the MLP Chemists to ensure accuracy and data integrity before distribution. The QA Officer reviews for accuracy all manual changes and data flagging along with audit trail software, function, and interruptions on a quarterly basis.

C2. Report to Management

The MLP team anticipates operating the MAAML on a near-continuous basis with management regularly apprised of project status. The QA Officer and Program Manager will

discuss major project issues as necessary. The QA Officer regularly reviews the results of instrument checks and QA/QC data. The MLP team sends quarterly assessment reports to the EPA Region 6 Project Manager for review of project progress.

D. DATA VALIDATION AND USABILITY

D1. Data review, verification and validation

Data review, verification, and validation form the integral parts of quality management for the MLP. The MLP team reviews all analytical data to verify the preliminary qualitative and/or quantitative results. The team also reviews the associated quality control data to ensure meeting all data quality objectives.

The QA Officer then reviews the data for any anomalies or non-conformances and identifies any potential data quality issue. The QA Officer then instructs MLP Chemists to investigate any anomalies for assignable causes prior to data reporting.

D2. Verification and Validation Methods

Data validation process includes series of quality control checks. Table 5 shows the quality control checks and acceptance criteria for MLP data.

Table 5: Quality Control Checks and Acceptance Criteria

Quality control check	Purpose	Frequency	Acceptance Criteria
Retention time check	To help assess retention time shift and optimize procession mentods	Bi-weekly or as needed based on performance.	100% of the compounds are identified correctly RT check standard
Calibration Verification Standard (CVS)	To assess instument drift and insure continued instrument calibration	Daily	70%-130% recovery compared to the curve for all target compounds
Method Blank	System background	Daily	FID: 1) Target compound concentrations ≤ 2.0 ppbV-C 2) TNMHC values ≤ 20.0 ppbV-C MS: Target compond concentrations ≤ 0.5 ppbV
Precision check	To assess analytical precision	Weekly	Target compounds <25%

The MLP team reviews GC/FID/MS data for abnormal values and validates the data with regard to the appropriate quality specifications, qualifying (flagging) any data not meeting the appropriate quality specifications.

D3. Reconciliation with User Requirements

The MLP team, Quality Assurance Officer, and Program Manager monitor the status of the MLP and review the data as regards the data quality objectives listed in Section A7 (replicate precision criteria within 25%, accuracy within 30%, and data recovery of 75% for every MAAML sampling trip). MLP personnel will inform the QA Officer of any deviation from the data quality objectives. The QA Officer will then both determine what action for MLP personnel to take to bring the data into compliance with the data quality objectives and inform the Program Manager of the action taken.

Appendix A

Responsibilities and Authorities of Personnel in Quality Assurance Mobile Laboratory Program



City of Houston

Bureau of Pollution Control and Prevention

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Responsibilities and Authorities of Quality Assurance Personnel

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Responsibilities and Authorities of Quality Assurance Personnel

1. Bureau Chief

The Bureau Chief is responsible for the operation of the BPCP. He disseminates information and policies to the staff as necessary. The Bureau Chief meets with the Program Manager of the Mobile Laboratory Program (MLP) to review operations. The Program Manager will confer with the Bureau Chief on all issues regarding operations that cannot be resolved at the Program Manager's level. The Program Manager makes operational decisions with input from the QA Officer, Operations Leader, and Chemists.

The Bureau Chief conducts a staff meeting with BPCP staff once a month to discuss the month's activities and upcoming plans. Relevant safety training issues are included in the meeting's agenda.

2. Program Manager

The Program Manager, responsible for the overall operation of the MLP, makes use of the collected data to respond to MLP specific requirements. Additionally, the Program Manager participates in various Technical Conferences and workgroups as well as maintaining communication with key EPA Region 6 personnel. The Program Manager often represents the Bureau in meetings and public outreach events. The Program Manager's responsibilities include planning and implementing proper operation of the mobile laboratory, procuring and replacing all monitoring instruments, handling personnel needs as well as their safety issues, implementing City policies, and addressing the other needs of the MLP. The Program Manager holds ultimate responsibility for the quality assurance of the all data obtained through the Mobile Laboratory Program and for the submission of all collected data to the EPA Region 6 Office as specified in the grant proposal and awarding letter.

The Program Manager acts upon current or on-going QA problems independently identified by the QA Officer that may require additional resources, personnel, or training. Then the Program Manager brings these problems to the attention of the Bureau Chief as necessary to ensure meeting all program objectives. This process ensures that management knows of any ongoing QA/QC issues and of the status of the corresponding corrective actions. The Program Manager works with the EPA Region 6 Office to develop better understanding of Houston's air quality problems.

With independent input from the QA Officer regarding Quality Assurance/Quality Control (QA/QC) procedures, the Program Manager meets with MLP staff on an individual and collective basis to ensure work proceeds as scheduled with implementation of all QA/QC procedures. The Program Manager may elevate any unresolved questions regarding the MLP to the Bureau Chief for resolution.

3. Quality Assurance Officer

The QA Officer maintains responsibility for all QA/QC procedures and their implementation. These procedures assure proper operation of the instruments and timely collection of valid data. The QA Officer discusses relevant questions with the Program Manager, Operations Leader, and Chemists and identifies potential concerns and solutions regarding data collection or operational protocols.

The QA Officer ensures that QA/QC checks and data collected by the mobile laboratory are performed in a timely manner and consistent with requirements, agreements, and policies of the BPCP and the EPA. The QA Officer's principal tasks involve monitoring the MLP from a QA/QC perspective to include such aspects as overseeing QA/QC procedures and documentation, data validation, data concerns, instrument checks, and evaluation of Standard Operating Procedures.

The MLP QA Officer may communicate with EPA Region 6 personnel such as the QA Manager for EPA Region 6 as necessary for project goal attainment.

The QA Officer reports directly and solely to the Program Manager to maintain independence of action and freedom from bias throughout the MLP. The QA Officer and the Program Manager work together and in concert with the Operations Leader and Chemists so that the MLP produces data of known quality.

4. Operations Leader

The Mobile Laboratory Operations Leader is the Team Leader for the MLP. The Operations Leader participates in the data review and validation process as the second of four review levels with peer review by the Chemists the first, monitoring by the QA Officer the third level, and Program Manager review the fourth and final level. The Operations Leader tracks instrument performance, certification, and problems. The Operations Leader oversees data collection and analytical methodologies, performs and reviews QA/QC checks on all instrumentation, prepares data files and reports, and assists in Chemist training.

Unresolved questions presented by Chemists on QA/QC check procedures and data validation go to the QA Officer for resolution.

5. Chemists

The MLP Chemists hold responsibility for the proper operation, calibration, maintenance, and documentation of the MLP instruments.

The MLP Chemists perform standard instrument checks such as calibrations and QA/QC checks that ensure the proper operation and valid data collection. The MLP Chemists also document instrument checks and diagnostics as well as other events of note. Documentation occurs in the instruments' daily logbooks, maintenance logs, instrument data files, and other relevant locations as listed in the QAPP.

The MLP Chemists immediately relay all deviations from acceptable instrument operation and/or data collection to the Operations Leader and the QA Officer.

Appendix B

REFERENCES

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2. Quality Management Plan for Mobile Laboratory Program. City of Houston, Bureau of Pollution Control and Prevention, Technical Service, March 2006.
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Appendix C

Bureau of Pollution Control and Prevention Standard Operating Procedure

TD-GC/FID/MS for Air Toxics Analysis in the Mobile Ambient Air Monitoring Laboratory (MAAML)

Revised by:

Youjun Qin – Chemist IV

Date

Approved by:

James Rhubottom – Chemist IV/Operations Leader

Date

Peter Chen – Chemist IV

Date

Donald Richner – Program Manager

Date

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Purpose

The purpose of this SOP is to document the analytical procedure for the measurement of volatile organic air toxics using TD-GC/FID/MS in the Mobile Ambient Air Monitoring Laboratory (MAAML). The data will provide an air quality database that will assist in tracking and monitoring emissions from industrial facility sources and automobile sources. The air toxics that are the primary focus of the MAAML's investigations are volatile organic compounds (VOCs) such as 1,3-butadiene and benzene known to cause serious health effects and are also the ozone precursors. This document covers system performance checks, sample loading, sample analysis, data acquisition, and data verification of the TD-GC/FID/MS.

Scope and Applicability

Instruments include the Agilent 6890N/5975C Gas Chromatograph/Mass Spectrometer with A Flame-Ionization Detector, the Markes CIA Air Server and UNITY2 Thermal Desorber. The primary focus of this SOP is the quantitation of organic air toxics such as 1,3-butadiene, benzene etc. The standard analyte lists and quantitation limits are provided in Table 3 and Table 1, respectively.

This document covers system performance checks, sample loading, sample analysis, data acquisition, and data verification and documentary. This procedure will allow for continuous measurements of ambient air samples, as well as analysis of collected samples in SUMMA[®] canisters and sample bags.

Personnel Qualification and Training

This document is intended for Chemists and Environmental Investigators working for the City of Houston Bureau of Pollution Control and Prevention in the Mobile Ambient Air Monitoring Laboratory. For the purposes of this document qualified personnel will be identified as operators. Operators require no certification but working knowledge of analytical instruments, basic chromatography, and mass spectrometry. All MAAML personnel must receive hands-on training with the MAAML equipment and related analytical instruments. All MAAML personnel must demonstrate working knowledge of the instrumentation through the completion of a Demonstration of Capability (DOC), to be administered by the Technical Services manager. The MAAML team is required to receive training in field sampling, defensive driving, first aid, and emergency procedures

Definitions

Calibration – A process of determining a mathematical response ratio to a set of known concentrations.

Calibration Verification Standard and Duplicate (CVS/CVSD) – A quantitative sample consisting of known concentrations of standard analytes, ex. Propane, 1,3-Butadiene and benzene. Analysis is used to verify analytical system accuracy.

Dilution Factor – A measure comparing the amount of a sample or standard and its diluent in a solution.

Flame Ionization Detector – Gas chromatographic detector used for hydrocarbon analysis

Linearity Range – The acceptable range of response for the quantitation of results. The upper acceptance for this range is the highest calibration point.

Method Blank – A sample consisting of zero air used to assess the potential contamination within an analytical system.

Method Detection Limit (MDL) – An analysis consisting of a series of known concentrations used to mathematically determine the threshold concentration for the minimum response. It is the minimum concentration of an analyte that can be measured and reported with a 99% confidence that the analyte concentration is greater than zero.

Percent Recovery – A calculation of a measure value compared to a theoretical value. The amount of a component which is recovered and detected from a known standard.

Precision – The measure of the reproducibility of a measure value

Response Factors (RF) – A measure which indicates a system's response to a known value, the ratio of the detector response to the amount of analyte in the calibration standard used for calibration in flame ionization detector and mass spectrometry.

Retention Time (RT) – The amount of time a specific compound resides in a chromatographic system before reaching the analytical detector.

Retention Time Verification Standard (RTS) – A sample with a blend of known compounds used to verify the location of those compounds in a chromatographic column.

Standard Deviation (STD) – A measure of the average distance of individual observations from the mean.

Relative Standard Deviation (RSD) – A measure of variability that is adjusted for the magnitude of observations involved.

Tentatively Identified Compounds (TICs) – Compounds detected in a sample that are not target compounds, internal standard, or surrogate compounds and are tentatively identified by mass spectral library searches, typically reported with estimated concentrations

Safety

All work must be performed in accordance with the appropriate health and safety procedures specified in the Houston Department of Health and Human Services Safety and Health Manual (May 2003).

Personal Protective Equipment

Personal protective equipment, including but not necessarily limited to eye protection, Nomex[®] suits, steel-toed shoes, gloves, and hearing protection must be worn and used as specified by HDHHS Safety and Health Manual. This includes all visitors, personnel, and contractors that are within the working scope of the MAAML.

Specific Safety Concerns or Requirements

Health and safety information can be obtained from the Material Safety Data Sheets (MSDSs) maintained by the laboratory. The MAAML presents potential electrical, physical, and chemical hazards. The following specific concerns or hazards are known:

- Chemicals to be used: methanol, acetone, methylene chloride, hydrogen, zero air, helium.
- Compressed gas cylinders are often heavy and hard to physically handle. All cylinders must be tightly secured via strap or chain to a sturdy, fixed structure. Never remove the safety cap on a cylinder while it is being moved. Cylinders must be handled using a cylinder dolly. Empty and full cylinders must be clearly marked. When attaching a regulator to a cylinder, use the appropriate CGA fitting. Check gas lines and fittings for leaks after cylinder or regulator replacement.
- Always unplug a heat traced line before maintenance and when disconnecting gas lines. Check for frayed or missing insulation before turning the power on.
- Electrical systems must be periodically checked for frayed wire, loose connections, or missing components. Never use electrical tape to repair frayed wires, or to join a spliced wire.
- If a circuit breaker is thrown, all instruments on that circuit must be turned off before power is restored. Only then may instruments be turned on one at a time to determine which instrument is causing the breaker to throw.
- Extreme heat and cold zones are found on the Thermal Desorber and analytical instruments. The Thermal Desorber uses an electrically cooled trap which can reach a temperature of -35°C during sample collection. The trap may climb to 325 °C during desorption. The gas chromatograph oven and FID may reach temperatures of up to 250°C. Avoid contact with the internal components of the instruments to avoid injury and burns. Cryogenic burn zones include the thermal desorber. Heated zones include the thermal desorber, GC oven, FID, and transfer lines.
- The enclosed space of the MAAML makes trip hazards present in the form of electrical and sampling lines. All such lines must be secured out of the main walkways or covered with protective strips.
- The zero air and hydrogen gas generators will be producing gas on a continuous basis. Hydrogen gas is flammable and can accumulate in a confined area. Do not allow hydrogen gas to collect in one area, and always maintain adequate ventilation.

- A posted list of emergency phone numbers, contacts, and personal protective equipment including gloves, safety glasses, and a first aid kit must be available inside the MAAML and in the garage.

Materials Used

The following is a list of the primary materials used in this procedure, which have a serious or significant hazard rating. This does not include all materials used in the sampling effort, or the sample matrices. Employees must review the information in the MSDS for each material before using it for the first time.

Material	Hazards	TCEQ Effects Screening Levels (ESLs) – long term	Signs or Symptoms of Exposure
Methanol	Flammable, Poison, Irritant	200 ppbv	Slight irritant to the mucous membranes. Toxic effects exerted upon nervous system, particularly the optic nerve. Symptoms of overexposure may include headache, drowsiness and dizziness. Methanol is a defatting agent and may cause skin to become dry and cracked. Sin absorption can occur; symptoms may parallel inhalation exposure. Irritant to the eyes.
Methylene chloride	Carcinogen, Irritant	7.5 ppbv	Causes irritation to respiratory tract, gastrointestinal tract. Strong narcotic effects with mental confusion, fatigue, nausea, vomiting and headache. Causes formation of CO in blood which effects cardio and central nervous system. Continued exposure man cause unconsciousness and death. Causes redness and pain on skin contact; liquid degreases the skin. May be absorbed thru the skin.
Acetone	Flammable, Irritant	250 ppbv	Inhalation may irritate respiratory tract. May cause coughing, dizziness, and headache. Irritating due to defatting action on skin; causes redness, pain, drying and cracking of the skin. Long term exposure may produce central nervous system depressions, narcosis, and unconsciousness.

Equipment and Supplies

Markes Air Collection System

- Markes CIA8 Air Server
- Markes UNITY2 Thermal Desorber

Agilent GC/FID/MS System

- Agilent Model 6890N network gas chromatograph with flame ionization detector (FID 210), dual EPA split/splitless inlets (112), a microfluid Dean's switch (888), pneumatics control module (309), LAN and 7683 interface
- Agilent Model 5975C Inert Mass Selective Detector (MSD) performance turbo EI mainframe with G3397A ion gauge controller

Reagents and Standards

- GC Carrier Gas – GC grade helium (He) or equivalent.
- MS Instrument Performance Check Compound – 4-Bromofluorobenzene (BFB).
- MS Tuning Compound – Perfluorotributylamine (PFTBA).
- Calibration Standards – 100 ppbV of standards containing compounds listed in Table 3.
- Analytical Internal Standards and Surrogates – 4-Bromofluorobenzene.
- System Purge Gas – UHP (ultra-high purity) helium.

Quality Control

Quality control (QC) samples are used to ensure that the data produced from a particular analytical source are of acceptable and consistent quality throughout the analytical procedure. QC samples are analyzed to assess precision and accuracy. They include method blanks, calibration samples and duplicates, laboratory control samples and duplicates, sample duplicates, surrogates, and internal standards. A summary of this criterion is found in Table 1.

Method Blank

The method blank (MB) is a control sample prepared using a well-characterized blank matrix (e.g. zero air) and using the same reagents used for sampling. As part of a QC batch, the method blank accompanies the samples through all steps of the analytical process. The MB is used to monitor the level of contamination introduced to a batch of samples as a result of handling in the laboratory. One MB must be processed within an analytical batch, normally analyzed daily before any samples are analyzed. The MB should not contain any confirmed analytes of interest > 2ppbc for FID, and >1.0 ppbV for MS. The sum of all target compounds must be < 20.0 ppbc. See Table 1 for a list of QC criteria.

Corrective Action for Blanks:

If a target analyte in the method blank exceeds the reporting limit, the method blank must be reanalyzed. If the reanalysis still fails the acceptance criteria, all samples that were analyzed within the batch must be re-sampled if possible. If re-sampling is not possible, then all associated samples must be flagged with a "B" flag on the appropriate analyte of interest, and possible invalidation of the data after review. A narrative should be added to the data to provide further documentation.

The following special situations may allow qualified data to be reported without reanalysis, but will require a non-conformance memo (NCM).

- If there is no analyte greater than the reporting limit in the samples associated with an unacceptable MB, the data may be reported with qualifiers.
- If the analyte concentration in the samples is greater than 10 times the MB concentration, the data may be reported with qualifiers.
- If the blank contamination is less than the concentration present in the samples and is less than $1/10^{\text{th}}$ of the regulatory limit, the data may be approved with qualifiers.

Any surrogates in the method blank must pass acceptance criteria. If the surrogates fail acceptance criteria, the data must be reviewed to determine if the MB has accurately demonstrated that the analysis is free of contamination; or if the MB matrix is creating a matrix effect that is altering the surrogate recoveries.

Calibration Verification standard and Duplicate (CVS/CVSD)

The calibration verification standard (CVS) is prepared by obtaining the known concentrations of target compounds to assess instrument accuracy. The CVS is analyzed daily with an acceptable recovery criterion of 70-130%. The CVS is routinely analyzed in duplicate (CVSD) and used to assess instrument precision from run to run. The CVSD is analyzed weekly. The acceptable precision criterion is an RPD of $\leq 25\%$. See Table 1 for a list of QC criteria.

Corrective Action for CVS/CVSD Recovery Failure:

If one or more analytes are outside of the established control limits, check instrument performance and reanalyze the CVS or CVSD. If the reanalysis does not resolve the failures, replace the CVS standard and reanalyze. If still not resolved, contact the Technical Services manager to assess whether re-sampling of any samples associated with the failing CVS is required. If the samples cannot be re-sampled, flag the data with the appropriate flag.

The following special situations may allow qualified data to be reported without reanalysis, but will require a non-conformance memo (NCM).

- If the CVSD recovery is high and the analytes were not detected in the sample, it may be possible to report the data with appropriate qualifiers.
- If the analyte concentrations are low, the RPD calculations may reach a statistical limit of precision. In such cases, surrogate recoveries may be used to provide evidence of accuracy control.

- In the case of all compounds of interest are within control, but non-target compounds are out of control, the CVS may be considered acceptable for reporting.

Corrective Action for CVS Precision Failure:

If established control limits for precision are not met, check the instrument performance. If the RPD is out of control, but both accuracy recoveries are within acceptance criteria, prepare an NCM and qualify the data.

Surrogates

Surrogates are organic compounds which are similar in chemical nature and behavior to the target analytes, but are not normally found in environmental samples. 4-Bromofluorobenzene is the surrogate for this procedure.

All samples in a batch are spiked with the surrogate to monitor the effects of both the matrix and the analytical process on accuracy. Surrogate spike recoveries must be evaluated by determining whether the concentration (measured as percent recovery) falls within the required recovery limits. Surrogate recoveries must be within established control limits. Document any failure on the final data reports.

Corrective Action for Surrogates:

The surrogate must be within established control limits for the CVS and method blank. Check all calculations to ensure that no errors were made. Check surrogate spiking solution for degradation, contamination, etc.

If not source of spiking failure is discovered, reanalyze the QC sample. If reanalysis does not confirm the original analysis, and is within acceptance criteria, then the problem was within the analyst's control and only the reanalyzed data should be reported. If the surrogate recovery still fails, reanalyze batch if samples are available.

If the surrogate fails acceptance criteria in a field sample, reanalyze the field sample if possible to check for matrix interference, i.e. humidity, interfering compounds, or interference from a prior analysis. Document the failure and note it on the final data report.

Internal Standards

Internal standards are added to each analytical standard, sample, and blank sample. These standards are only used for the mass spectrometer detector. The acceptance criteria for each internal standard must be $\pm 50\%$ recover of the internal standard area from the calibration verification standard (CVS). The acceptance criteria for each internal standard's retention time in every analysis must be within ± 20 seconds of the internal standard retention time from the continuing calibration standard.

Corrective Action for Internal Standards:

If internal standard are outside acceptance criteria, check instrument performance and the internal standard spiking standard for degradation. If unresolved, search for possible matrix effects, including coelutions, interferences, excess moisture, et al. Reanalyze the sample, and if still outside of control limits, issue an NCM if interference is suspected.

Retention Time Verification Standard (RTS)

The RTS is used to assess the qualitative ability of the system to identify peaks in a chromatogram with FID detector. The sample is composed of targeted compounds of FID spiked near the mid-point concentration of the calibration range. The RTS should be sampled after installation of new column and then as needed based on performance. Failure of the system to correctly identify these RTS compounds will require instrument optimization by the operator.

Calibration and Standardization

Initial Calibration Verification and Curve Fits

GC/FID

An initial calibration curve (ICAL-FID) consists of a minimum of three concentration levels that are analyzed to determine in working linear range of the analytical system for each compound. The concentration of the low point should be at or below the reporting limit.

The calibration curve correlation coefficient (r) must be ≥ 0.995 or an RSD of RFs $< 20\%$. If any curve fits fail the acceptance criteria, check the system performance, and repeat analysis of outlying points.

GC/MS

An initial calibration curve (ICAL-MS) consists of five concentration levels (1, 5, 10, 20 and 40 ppbv) that are analyzed to determine in working linear range of the analytical system for each compound. The concentration of the low point should be at or below the reporting limit.

The calibration curve correlation coefficient (r) must be ≥ 0.995 or RSD of RFs $< 30\%$, with two exceptions of $< 40\%$. If any curve fits fail the acceptance criteria, check the system performance, and repeat analysis of outlying points.

Initial Calibration Verification:

The initial calibration verification (ICV) is a secondary source standard containing target analytes, and is analyzed immediately after initial calibration. For each analyte, a percent recovery is calculated using the average response factor. Acceptance criteria is provided as guidance as $\pm 35\%$. If the ICV fails acceptance criteria, reanalyze ICV and check instrument performance. If the ICV still fails, check ICAL analyses for problems or statistical anomalies.

Daily Calibration Verification (CVS)

Every 24 hours of operation, a calibration verification standard (CVS) must be analyzed to assess instrument performance and to verify the response factors generated from the ICAL. The CVS is a standard containing known amounts of target analytes that is routinely spiked in the mid-range of the calibration linearity range. The percent difference (%D) is calculated between the CVS RF from the ICAL average RF. In general, %D must be within $\pm 30\%$.

Calibration Verification Standard Failure:

As long as less than 10% of all analytes in the CVS fail the acceptance criteria, continue the analysis with the failing compounds flagged appropriately. If more than 10% of all analytes fail the acceptance criteria, check instrument performance and reanalyze the CVS. If the CVS still fails, corrective maintenance must be performed.

Procedure

Method Summary

VOCs are monitored using the Markes Thermal Desorber, and Agilent GC/FID/MS system. The instruments consist of a gas chromatograph equipped with flame ionization and mass spectrometry detectors. The system uses a Markes U-AIRSV to collect the ambient air samples or induce the standard samples.

The system draws ambient air into the Markes Thermal Desorber at a specified rate. Excess moisture in the sample is removed by a Nafion[®] based drying membrane. The dry sample is collected in an electrically cooled cold trap in the thermal desorber. The sample is concentrated on the cold trap to achieve high sensitivity for very low concentrations of air toxics. The preconcentrator is then rapidly heated to thermally desorb the sample, and then the carrier gas flow is reversed to back flush the VOCs into the gas chromatograph. Due to the wide boiling point range of the VOCs, the GC is equipped with dual columns; Plot column for light compounds and BP1 column for heavier compounds. The hydrocarbons with C₁ through C₃ eluted from BP1 column in early period are switched to Plot column by Dean's switch. They are detected by the flame ionization detector. The high boiling point materials from C₄ through C₁₀ eluted late from BP-1 column are detected using mass spectrometry. An overview of the sample path for the system is shown in Figure 1.

Instrument Preparation

GC/FID

Each new column used for this method must undergo a 72-hour retention time study. Retention time windows must be calculated for each analyte on each GC column. Three injections of standard are made throughout the course of a 72-hour period. The standard deviation of the three absolute retention times is calculated for each single component. In the case where the standard deviation for a particular compound is zero, or less than 1.8 seconds, the default of 1.8 seconds per SW-846 will be used as the retention time window.

The retention time of each analyte, as established by the daily calibration check standard, plus or minus three times the standard deviation of the absolute retention times of the 72-hour retention time window study, defines the daily retention time window. Six times the standard deviation is used for instruments with electronic pressure control (EPC). Retention time windows greater than 1.5% indicate a problem with the system and corrective action should be taken.

Check that the FID is lit. A flame will be indicated by the condensation on the metal object held above the FID chimney. If the FID is not lit, it can be lit with either the instrument's auto-igniter or a coil lighter.

Verify that there is communication to the computer, and create an analytical sequence in the ChemStation software, being sure to use the current methods and correct report formats. Include all QC and samples to be analyzed.

Download the sequence to the data interface or data logger. Be sure to download the next sample to be analyzed.

GC/MS

An autotune may be used as a diagnostic tool in troubleshooting the mass spectrometer (MS). It also establishes the optimal voltages in the ion source. An autotune must be performed after major maintenance to the mass spectrometer. The settings must be compared to the last autotune that was performed. Significant difference may indicate a problem with the mass spectrometer. Once the autotune is completed, a maximum sensitivity autotune is completed and stored with the name as the date performed, e.g. Jan0107.u. The resulting tune report is reviewed and compared to previous reports. Significant differences may require recalibration of the GC/MS.

The filament current is evaluated by ramping the repeller using different filament current settings. The curves that are generated represent an acceptable filament current when there is good separation of the peak maxima for all three masses (69, 219, 502) from the tuning compound, PFTBA.

The sensitivity of the mass spectrometer may be adjusted by increasing the voltage on the electron multiplier. The need to perform this task is determined by examining the area of the internal standards and comparing them with those generated during the last detection limit study. If the areas are less than 50% of those found in the detection limit study, voltage may be added to the multiplier to correct for the loss of sensitivity.

A daily check of the instrument tune is done by evaluating the 4-bromofluorobenzene (BFB) from the first QC sample that passes its acceptance criteria at the beginning of the sequence. The spectrum of the full BFB is averaged and a background scan is subtracted before evaluation. The header "tuner" is selected under which the task of "evaluate BFB to screen" is selected. The resulting report contains the tune acceptance criteria that must be met in order to analyze samples. See Table 2.

Verify that there is communication to the computer, and create an analytical sequence in the ChemStation software, being sure to use the current methods and correct report formats. Include all QC and samples to be analyzed.

Instrument Settings

The table below shows the Markes U-AIRSV and Agilent GC/MS/FID settings for use in the ozone precursor analysis:

GC Function Key	GC Parameter	Default Method
Oven Programming	Temp 1	45 °C
	Time 1	15.0 min
	Rate 1	6 °C/min
	Temp 2	170 °C
	Time 2	0.0 min
	Rate 2	15.0 °C/min
	Temp 3	200 °C
	Time 3	6.0 min
	Rate 3	END
TD Programming (ambient sample)	Sample rate	12.5 mL/min
	Sample time	40.0 min
	Trap temp	-15 °C
	Purge	2.0 min
	Purge rate	10 mL/min
	Desorb time	3.0 min
	Desorb temp	325 °C

Sequences

A sequence file is a table of instructions used by the Markes U-AIRSV or GC/FID/MS system to control collection, analysis, and interpretation parameters. For routine analysis, the sequence files must be created for Markes U-AIRSV and GC/FID/MS system separately, and the files must be correlated with each other to maintain sample and data integrity. An internal standard is added to an ambient (calibration, blank, etc) sample before the sample is desorbed into GC.

Each row in the sequence for Markes U-AIRSV (Figure 4) corresponds to one set of instructions for a sample to be collected, including the number of sample, the type of sample, the instrument method (Figure 5) used for the sample collection and channel of sample.

Sample Type	Channel	Method Name
Blank	3	Airserver_method_blank(500c).mth
45 compound standard	1	Airserver_50cc(10ppb_mod).mth
16 compound standard	6	Airserver_50cc(10ppb_mod).mth
Internal standard	2	Airserver_Intenalstand(IS_5ppb).mth
Ambient	4	Airserver_500c(sample_mod).mth
Canister or bag	5, 7 & 8	Airserver_500c(sample_mod).mth

Each row in the GC/FID/MS sequence (Figure 6) corresponds to one set of instructions for each sample analyzed to include sample type, process method used for raw data interpretation, and the filename for the raw data files and analysis result files.

Process Methods

Parameters that define what kind of sample (ambient air, standard or blank) are collected and how raw data are interpreted are contained in the analytical systems' process methods. Since the analytical system in the MAAML is a dual column sampler with a separate collection instrument, three methods are required. EnviroQuant ChemStation and the Markes U-AIRSV use these methods to take ambient air samples or standard samples, define integration principles, identify peaks, and calculate compound concentration from peak area.

Data File Nomenclature

During analysis, information is continually recorded in a raw file (*.raw). This file contains information such as sample acquisition time, FID response, and MS response. Once the sample run is complete, the raw file is closed. Its information can then be used by ChemStation to process the data into result (*.rst), or text, (*.txt) files. ChemStation uses the data stored in the raw files to analyze information and create results, or text files. The result files yield interpreted information such as component name, concentration, and elution time. The text files are the same information in an easily transferable electronic format, e.g. ASCII or Excel.

Filenames have two parts: the file extension which defines how the information is presented, and the root file name. The root file name gives each analysis a unique identifier which provides information as to its origin. See table below for file nomenclature.

Example: TSYMMDDHH

T = Sample Type	B C D M Q A T X	Method Blank (MB) Daily Calibration Verification Standard (CVS) Method Detection Limit (MDL) Initial Calibration Verification (CAL) Retention Time Study (RTS) Ambient Air Sample Audit Sample Bad or Test Sample
S = Site ID	X	Garage
YY= Year	#	2008 = 08
MM = Month	#	Jan. = 01
DD = Date	#	1 st = 01
HH = Hour	#	0:00 = 00

Sample Analysis

Create a short sequence in both the Markes and Agilent systems. A method blank, a calibration and a calibration duplicate are three top samples for each short sequence.

Appropriate sample methods have to be used for various samples in the sequence.

Attach the appropriate QC standards to the sample ports on the Markes air server.

Open all canister or cylinder valves and check all pressure gauges.

Start Markes and Agilent systems using the sequences.

Close satellite standard containers or cylinder after calibration sample desorb.

After the calibration verifications and method blanks are completed, run the "qedit" program in ChemStation to make sure the peaks are correctly identified and the baselines are drawn.

Save any changes made and regenerate the summary report and then quantify the calibration and blanks samples.

If QC meets all acceptance criteria, MAAML will analyze ambient samples, canister samples or bag samples with another blank sample and calibration sample run after every 23 ambient samples.

Check all instruments and create a summary sequence for field sampling, record it in the instrument logbooks, and include sample specific information such as location, field ID, injection volume, raw data file name, daily CVS sample, and blank.

Data Analysis, Qualifiers, and Calculations

Data Analysis

A trained analyst may perform manual changes in the instrument data. The mathematical algorithms used to automatically integrate the sample peaks are not entirely accurate. Manual integrations may be performed to change those misshapen integrations into an optimized interpretation. The altered data must be saved with a different file extension to demonstrate that a manual integration was performed. For mass spectrometry data integrations using ChemStation, the audit trail function must be turned on at all times. All data must be transferred in the AIM server for storage and immediate public display. Data in which manual integrations were performed must be redistributed through the AIM server for storage.

Qualifiers

While reviewing the data, the operators and reviewer may flag any data that does not comply with the appropriate quality specifications with the appropriate qualifiers. The following flags that include, but are not limited to, may be applied to the data.

Flag	Definition
B	Analyte detected in method blank above 0.5 ppbv and analysis result is <10 times the value in the method blank
I	Interference or coelution suspected
NA	Not analyzed/Not available
C	Daily calibration sample does not meet the criteria
D	Duplicate calibration sample does not meet the criteria
ND	Not detected
Q	Result does not meet specification
U	Result less than sample specific method detection limit (MDL)
J	Result higher than or equal to MDL and less than the reporting limit (the lowest concentration for initial calibrations – 1 ppbv)

11.3 Calculations

Relative Percent Difference (RPD):

$$RPD = \frac{|x_1 - x_2|}{\left(\frac{x_1 + x_2}{2}\right)} * 100$$

Where:

x_1 = analytical % recovery

x_2 = replicate % recovery

Percent Recovery:

$$\%R = \frac{[MeasuredConcentration]}{[TheoreticalConcentration]} * 100$$

Response Factor for MS:

$$RF = \frac{(A_x C_{is})}{(A_{is} C_x)}$$

Where:

A_x = area of the characteristic ion for the compound being measured

A_{is} = area of the characteristic ion for the specific internal standard

C_{is} = concentration of the specific internal standard ($\mu\text{g/mL}$)

C_x = concentration of the compound being measured ($\mu\text{g/mL}$)

Average Response Factor for MS:

$$\overline{RF} = \frac{\sum (RF_1 + RF_2 + \dots RF_n)}{n}$$

Where:

RF_1 = response factor for first calibration point of a compound

RF_2 = response factor for second calibration point of a compound

RF_n = response factor for last calibration point of a compound

n = total number of calibration points

Standard Deviation:

$$s = \sqrt{\frac{\sum_{i=1}^n (x_i - \bar{x})^2}{n-1}}$$

Where:

n = total number of measurements in the set

x = individual measurements

\bar{x} = measured mean for the set

Canister Dilution Factor:

$$CanisterDF = \frac{PF - PI}{PT + 14.7(psig)}$$

Where:

PF = canister pressure after sampling (psig)

PI = canister pressure before sampling (psig)

PT = canister pressure after pressurization with diluent gas (psig)

Concentration of Analyte in a Sample Using Average Response Factor for MS:

$$Concentration = \frac{(A_x)(C_{is})(DF)}{(A_{is})RF}$$

Where:

A_x = area counts of characteristic ion for compound being measured

C_{is} = concentration of internal standard injected ($\mu\text{g/L}$)

A_{is} = area counts of characteristic ion for the internal standard.

Calibration Factor (CF) for FID:

$$CF = \frac{PeakArea}{Concentration}$$

Sample Concentration for FID:

$$PeakConcentration = \frac{PeakArea}{CalibrationFactor}$$

Method Detection Limit:

$$MDL = (S)(t)$$

Where:

S = standard deviation of the replicate analyses

t = students' t value for 99% confidence level and a standard deviation estimate with n-1 degrees of freedom

Method Performance

Training

- The analyst must complete the laboratory safety orientation training that includes, but is not limited to, chemicals, PPE requirements, and electrical safety.
- The analyst must read and understand this SOP.
- The analyst must have a completed training record approved by the Program Manager.

Responsibilities

Operator

The operator shall:

Daily:

- Verify proper system operating status,
- Verify the operation of the modem and data logger,
- Ensure that the analytical systems are functioning and collecting data,
- Review the daily calibration verification standard and method blank results,
- Check the peak identification, integration, and general chromatography of all samples collected,
- Optimize the methods if necessary,
- Verify BFB tuning requirements,
- Update electronic and written logbooks,

Weekly:

- Analyze the second source laboratory control standard (LCS) in duplicate (LCSD),

Bi-weekly

- Review and update sequence files,
- Check gas generation stations

Monthly:

- Verify all data archival,
- Routine data backup to CD/R/RW,
- Perform any computer or instrument maintenance as necessary.

12.2.2 Lab/Technical Manager

The lab/technical manager shall:

- Certify that the project specification are being met,
- Ensure that each operator has been properly trained in its use and has the required experience to perform this procedure,
- Ensure that this training/experience is documented,
- Periodically review all logs and logbooks documenting this review.

Waste Management

Waste generated during the performance of this procedure must be disposed of in accordance with the City of Houston Waste Management Plan. The waste management coordinator should be contacted if additional information is required.

Laboratory personnel assigned to perform hazardous waste disposal procedures must have a working knowledge of the established procedures and practices of the City of Houston. They must have training on the hazardous waste disposal practices upon initial assignment to these tasks, followed by annual refresher training.

References, Deviations and Clarifications

References

- TCEQ. Revision 12, May 2003. PAMS Network Quality Assurance Project Plan for Monitoring Texas. TCEQ. Austin, TX
- TCEQ, May 2005. Standard Operating Procedure, Perkin-Elmer Auto Gas Chromatography for VOC Ozone Precursor Analysis
- EPA, October 2003. Compendium Method TO15, "The Determination of Volatile Organic Compounds (VOCs) in Air Collected in SUMMA[®] Canisters and Analyzed by Gas Chromatography/Mass Spectrometry (GC/MS)"
- 40 Code of Federal Regulations, Part 136, Appendix B.

Tables and Figures

Table 1: Summary of Calibration and QC Analyses

Table 2: BFB Key Ions and Abundance Criteria

Table 3: Analyte Lists and Quality Control

Figure 1: Sample Path

Figure 2: GS/MS and Unity2 cycle chart

Figure 3: Elution sequences for FID and MS

Table 1: Summary of Calibration and QC Analyses

Calibration & QC Analyses	Description	Frequency	Acceptance Criteria	Corrective Action
Initial Calibration (ICAL)	FID: 5-point calibration MS: 5-point calibration	Annually or when calibration verification fails to meet acceptance criteria	FID: calibration curve correlation coefficient (r) ≥ 0.995 or an RSD of RFs $< 20\%$. MSD: calibration curve correlation coefficient (r) ≥ 0.995 or an RSD of RFs $< 30\%$, with two exceptions of $< 40\%$.	1. Reanalyze concentration not meeting criteria 2. Troubleshoot instrument
Demonstration of Capability (DOC)	Quadruplicate analysis of second source standard	1. Initial method setup 2. For each new analyst prior to analysis of any samples	Mean Accuracy: % Recovery $\pm 35\%$	1. Verify calibration with second source standard 2. Troubleshoot instrument.
Calibration Verification Standard (CVS)	Standard for assessment of instrument accuracy containing analytes of interest	Daily	70%-130% recovery	1. Repeat CVS 2. Troubleshoot 3. Recalibrate
Method Blank (MB)	Canister with humidified UHP air to assess background	Daily	FID: 1. Target compound concentrations ≤ 2.0 ppbc 2. TNMHC values ≤ 20.0 ppbc MS: Target compounds ≤ 0.5 ppbV	1. Reanalyze MB 2. If not resolved, reanalyze all samples 3. If reanalysis not possible, flag all data <ul style="list-style-type: none"> If no analyte $> RL$ in samples, data may be reported without flags If analyte concentration in sample is > 10 times the MB concentration, may be reported with qualifiers 4. Troubleshoot instrument.
Calibration verification Standard	Standard containing analytes of	Weekly	Precision: $< 25\%$	1. Reanalyze CVSD 2. Reprep CVS

Duplicate (CVSD) for Precision	interest analyzed in duplicate			standard and analyze 3. Troubleshoot instrument.
Retention Time Standard (RTS)	Standard containing target compounds identified by FID.	Initial study after installation of a new column and then bi-weekly or as needed based on performance	Retention time window is set at plus or minus three times the standard deviation of the absolute retention times for the 72-hour study	1. Identify and correct source of problem. 2. Repeat study.
BFB Tuning Check	Evaluation of 4-bromofluorobenzene (BFB) peak in the calibration verification.	At the beginning of each analytical sequence	Must meet ion abundance criteria listed in Table 2.	1. Evaluate BFB in method blank 2. Re-tune and reanalyze BFB 3. Troubleshoot, retune if necessary.
Internal Standards	Three internal standard added to each sample, standard, and blank	All samples, standards, and blanks	Measured area must be $\pm 50\%$ of internal standard area from the calibration verification standard (CVS)	1. Reanalyze sample if out of specification 2. Identify and correct problem 3. Recalibrate
Analytical Surrogate	One surrogate compounds are added to each sample, standard, and blank	All samples, standards, and blanks	Accuracy: 50%-150% recovery	1. Reanalyze sample for matrix effect evaluation 2. If matrix specific, flag data 3. Troubleshoot instrument

Table 2: BFB Key Ions and Abundance Criteria

Mass	Ion Abundance Criteria
50	8.0 to 40% of mass 95
75	30 to 66% of mass 95
95	Base peak, 100% relative abundance
96	5.0 to 9.0% of mass 95
173	<2% of mass 174
174	50 to 120% of mass 95
175	4.0 to 9.0% of mass 174
176	93 to 101% of mass 174
177	5.0 to 9.0% of mass 176

Table 3: Analyte Lists and Quality Control - Expanded Analyte List

Name	CAS No.	MDL (ppbv)
Ethane	74-84-0	0.1
Ethylene	74-85-1	0.1
Propane	74-98-6	0.1
Dichlorodifluoromethane	75-71-8	0.8
Propylene	115-07-1	0.1
Acetylene	74-86-2	0.1
Methyl chloride	74-87-3	0.3
1,2-Dichlorotetrafluo...	76-14-2	0.4
Vinyl chloride	75-01-4	0.2
1,3-Butadiene	106-99-0	0.4
n-Butane	106-97-8	0.2
Bromomethane	74-83-9	0.2
Ethyl Chloride	75-00-3	0.3
Trichlorofluoromethane	75-69-4	0.1
n-Pentane	109-66-0	0.1
1,1-Dichloroethylene	75-35-4	0.1
Methylene Chloride	75-09-2	0.3
1,1,2-Trichlorotrifluo...	76-13-1	0.3
1,1-Dichloroethane	75-34-3	0.2
2-methylpentane	107-83-5	0.1
1-Hexene	592-41-6	0.1
Cis-1,2-Dichloroethylene	156-59-2	0.3
Hexane	110-54-3	0.1
Chloroform	67-66-3	0.5
1,2-Dichloroethane	107-06-2	0.4
1,1,1-Trichloroethane	71-55-6	0.6
Benzene	71-43-2	0.2
Carbon Tetrachloride	56-23-5	0.8
1,2-Dichloropropane	78-87-5	0.5
Trichloroethylene	79-01-6	0.2
Cis-1,3-dichloropropene	10061-01-5	0.4
Trans-1,3-Dichloropropene	10061-02-6	0.2
1,1,2-Trichloroethane	79-00-5	0.3
Toluene	108-88-3	0.2
1,2-Dibromoethane	106-93-4	0.2
Tetrachloroethylene	127-18-4	0.3
1,1,1,2-tetrachloroethane	630-20-6	0.2
Chlorobenzene	108-90-7	0.1
Ethylbenzene	100-41-4	0.1
m/p-Xylene	108-38-3 & 106-42-3	0.3
Styrene	100-42-5	0.1
o-Xylene	95-47-6	0.1
1,1,2,2-Tetrachloroethane	79-34-5	0.3
Cumene	98-82-8	0.2
1,3,5-Trimethylbenzene	108-67-8	0.1
1,2,4-Trimethylbenzene	95-63-6	0.1
1,3-Dichlorobenzene	541-73-1	0.1
1,4-Dichlorobenzene	106-46-7	0.1
1,2-Dichlorobenzene	95-50-1	0.2
1,2,4-Trichlorobenzene	120-82-1	0.4
Hexachloro-1,3-Butadiene	87-68-3	0.3

Surrogate

- Bromofluorobenzene (BFB)

Internal Standards

- Bromochloromethane
- 1,4-Difluorobenzene
- Chlorobenzene-d5

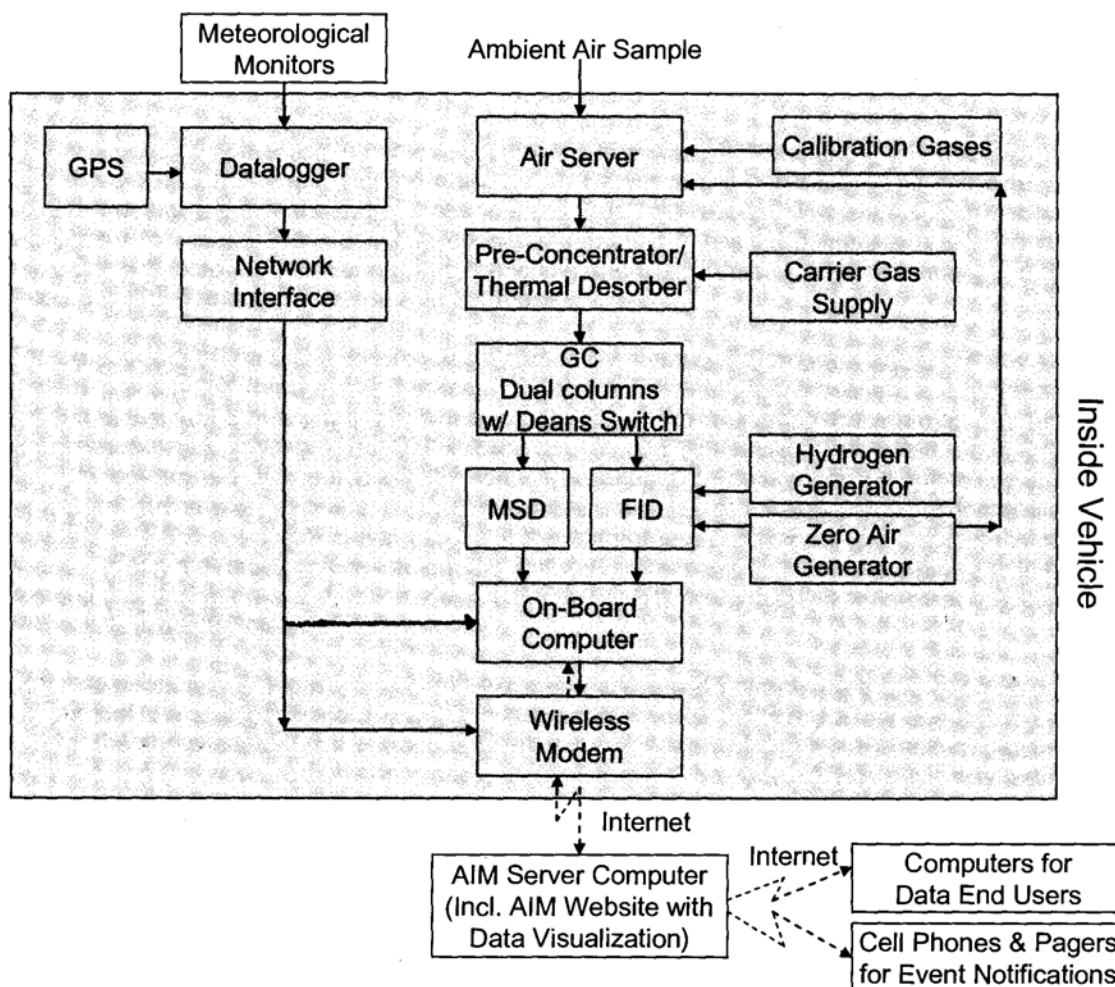


Figure 1: Sample Path

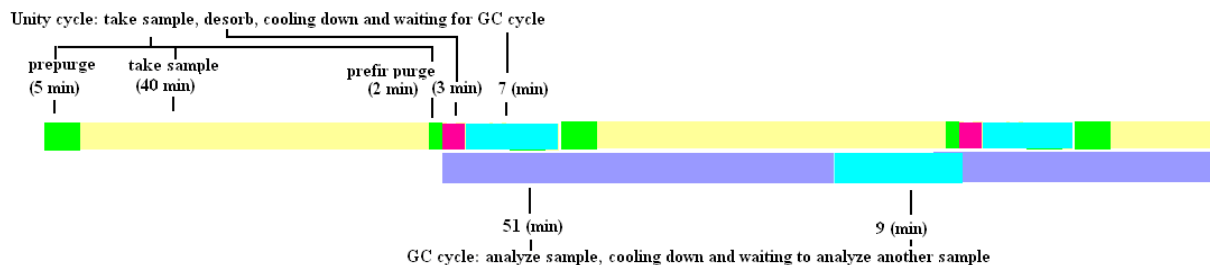


Figure 2: GS/MS and Unity2 cycle chart

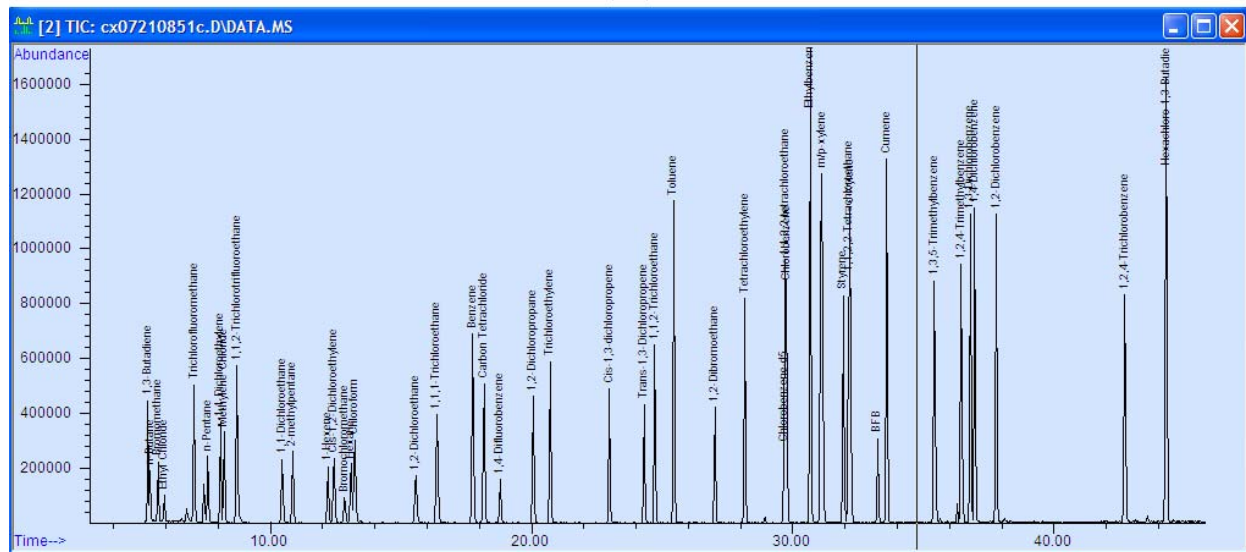
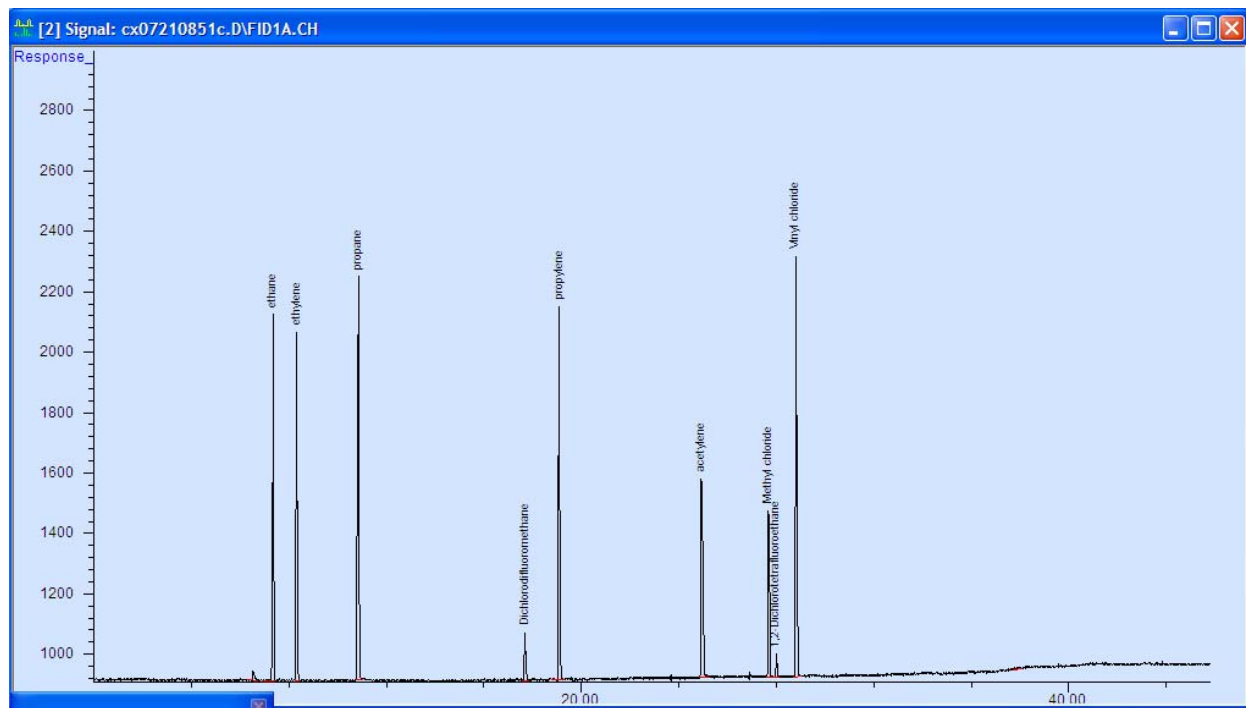


Figure 3: Elution sequences for FID and MS

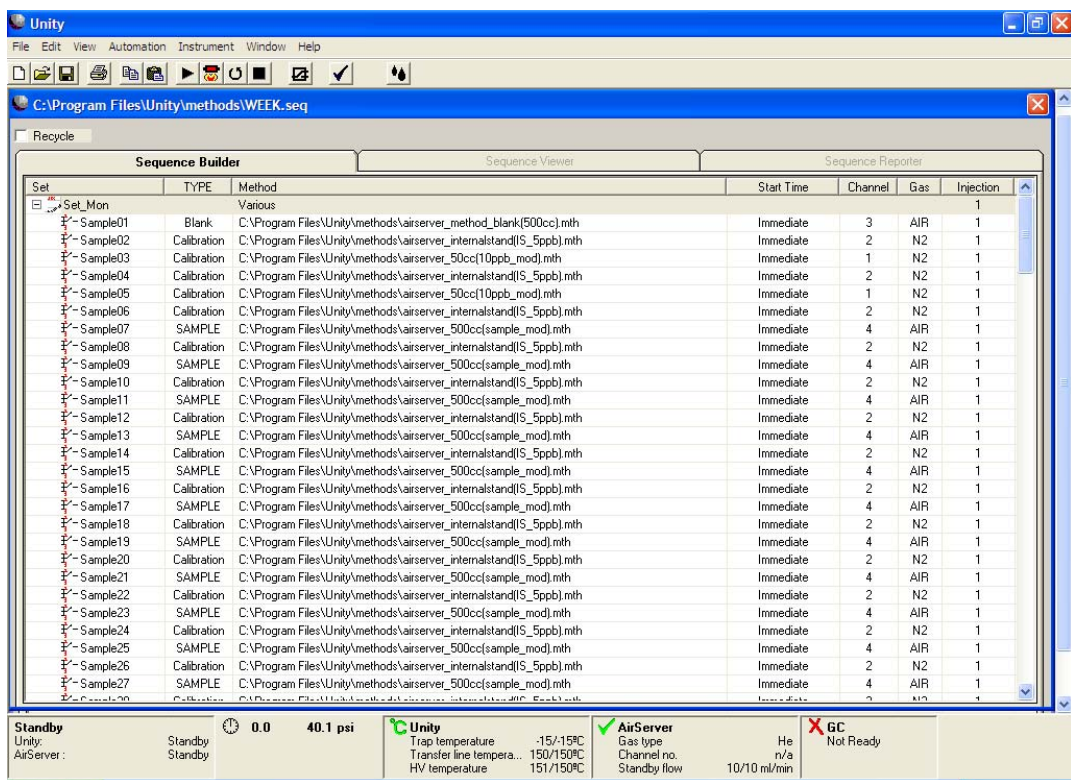


Figure 4: Control sequence for UNITY2

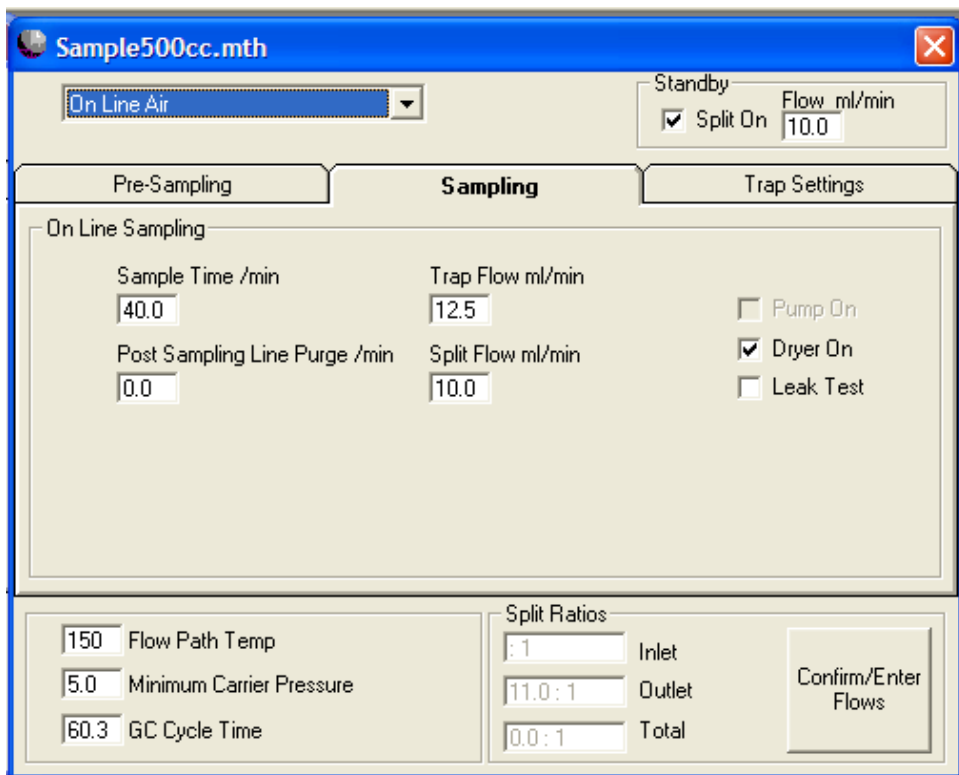


Figure 5: Sample Method for UNITY2

Instrument #1 / Environmental - MS063008.M / TEST2.S

Method Instrument Sequence View Abort Checkout Security Control Window Help

Instrument Control

Idle Sample Name: 1 Data File: bx072209k.d Run Time: 45.83

Sequence Method Instrument

150 330 100

Sample Log Table

Data Path: C:\MSDCHEM\1\DATA\2008\Jul23 Browse... Method Path: C:\MSDCHEM\1\METHODS Browse...

	Type	Vial	Sample	Method / Keyword	Data File	Comment / KeywordString	Multiplier	Level	Up
1	Blank	1 test	MS063008	bx07230801	Blank	1.00000	No Up		
2	Calibration	1 test	MS063008	cx07230802	Blank	1.00000	No Up		
3	Calibration	1 test	MS063008	cx07230803	Blank	1.00000	No Up		
4	Sample	1 test	MS063008	ax07230804	Blank	1.00000	No Up		
5	Sample	1 test	MS063008	ax07230805	Blank	1.00000	No Up		
6	Sample	1 test	MS063008	ax07230806	Blank	1.00000	No Up		
7	Sample	1 test	MS063008	ax07230807	Blank	1.00000	No Up		
8	Sample	1 test	MS063008	ax07230808	Blank	1.00000	No Up		
9	Sample	1 test	MS063008	ax07230809	Blank	1.00000	No Up		
10	Sample	1 test	MS063008	ax07230810	Blank	1.00000	No Up		
11	Sample	1 test	MS063008	ax07230811	Blank	1.00000	No Up		
12	Sample	1 test	MS063008	ax07230812	Blank	1.00000	No Up		
13	Sample	1 test	MS063008	ax07230813	Blank	1.00000	No Up		
14	Sample	1 test	MS063008	ax07230814	Blank	1.00000	No Up		

Sheet1

OK Cancel Help

Figure 6: Control sequence for GC/MS

Bureau of Pollution Control and Prevention Standard Operating Procedure
Determination of Air Toxics in SUMMA Canisters and Tedlar Bags by
TD-GC/FID/MS in the Mobile Ambient Air Monitoring Laboratory (MAAML)

Revised by:

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Date

James Rhubottom – Chemist IV/Operations Leader

Date

Approved by:

Dr. Peter Chen – Chemist IV

Date

Patricia Beltz – Quality Control Officer

Date

Dr. Wei-Yeong Wang – Technical Services Chief

Date

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1.0 Purpose

This SOP documents the sampling and analytical procedures for the measurement of air toxics samples as collected in both Tedlar bags and SUMMA[®] passivated canisters via TD-GS/FID/MS in the Mobile Ambient Air Monitoring Laboratory (MAAML). The air toxics of primary interest center on volatile organic compounds (VOCs) such as 1,3-butadiene and benzene, known ozone precursors capable of causing serious health effects. This document covers the procedures for Tedlar bag and SUMMA[®] passivated canisters to include cleaning, sampling, and delivering along with the procedures for the TD-GC/FID/MS system performance checks, sample loading, sample analysis, data acquisition, and data verification.

2.0 Scope and Applicability

The canister sampling apparatus includes SUMMA[®] passivated canisters, passive air sampling kits, pressure gauge, and canister cleaning system. The Tedlar bag sampling apparatus includes vacuum boxes, Teflon and Tygon tubing, Tedlar bags, and sampling pumps. The analytical instrumentation includes the Agilent 6890N/597C Gas Chromatograph/Mass Spectrometer with a Flame-Ionization Detector, the Markes U-AIRSV Air Server, and Unity Thermal Desorber. Tables 3 and 1, respectively, reflect the standard analyte lists (51 compounds) and quantitation limits.

This document covers the procedures for Tedlar bag and SUMMA[®] passivated canisters to include cleaning, sampling, and delivering along with the procedures for the TD-GC/FID/MS system performance checks, sample loading, sample analysis, data acquisition, and data verification.

3.0 Sample Preservation, Containers, Handling, and Storage

The Tedlar bags most commonly used for sampling have a 10-liter volume. Upon sampling completion, the Field Sampler stores the Tedlar bags in either a clean cooler or a trash bag to prevent photo-degradation.

Note: Conduct sample analysis within 48 hours, as after this time compounds may escape or may undergo alteration.

4.0 Interferences and Potential Problems

Contamination remains a major concern since many of the compounds in question will be present in the parts per billion range. In order to minimize the risk of cross contamination, Field Samplers and Operators should consider the following factors:

Proximity of the bags to the source(s) of potential contamination during transportation and storage could pose a problem since the farther away from the source(s), the less likely the bags will encounter the chances for external contamination.

Attach bags to fittings with clean Teflon tubing only.

Once the Field Sampler or Operator has collected the bag sample, affix the sample label to the edge of the bag. Adhesives found in the label may permeate the bag if placed on the body of the bag. Fill out labels with a ballpoint pen as permanent markers contain volatile compounds that may contaminate the sample.

Due to the chemical structure of Tedlar, highly polar compounds will adhere to the inner surface of the bag. In addition, low molecular weight compounds may permeate the bag. Field Samplers and Operators should employ real-time monitors such as the organic vapor analyzer, photoionization detector, and combustible gas indicator as screening devices prior to sampling. Next, the Field Samplers or Operators should write the information gathered on the sample label to inform the Operators performing the sample analysis.

While the Tedlar bag sampling system remains straightforward and easy to use, Field Samplers and Operators should take note of the following things when sampling:

Ensure an airtight seal between the top and bottom half of the vacuum box in order for the system to work.

Check the O-ring gasket to ensure its placement with the proper fit. Stretched out O-rings will not remain in place, thus requiring constant realignment.

Check that all the fittings associated with the vacuum joints are securely in place. The fittings can loosen when inserting the valve stem into the Teflon tubing.

Occasionally, a corner of the Tedlar bag will stick out between the two halves of the vacuum box causing a poor seal. Since the bags will hold only a given volume, over-inflation will cause the bags to burst.

5.0 Personnel Qualification and Training

This document serves as the primary operational guide for all Chemists and Environmental Investigators working for the City of Houston Bureau of Pollution Control and Prevention. For the purposes of this document, qualified personnel have the designation of either Field Samplers or GC/FID/MS Operators. GC/FID/MS Operators require no formal certification but must possess a working knowledge of analytical instruments, basic chromatography, and mass spectrometry. All Field Samplers must receive hands-on training with SUMMA[®] passivated canisters, passive air sampling kits and sampling methods for grab sample and integrated sample along with training in the use of Tedlar bags and affiliated equipment for the collection of grab (direct) and integrated (indirect) ambient air samples. All GC/FID/MS Operators must receive hands-on training with the MAAML equipment and related analytical instruments. GC/FID/MS Operators must demonstrate working knowledge of the instrumentation through the completion of a Demonstration of Capability (DOC), administered by the Technical Services Manager.

6.0 Definitions

Calibration – A process of determining a mathematical response ratio to a set of known concentrations.

Calibration Verification Standard and Duplicate (CVS/CVSD) – A quantitative sample with known concentrations of standard analytes, ex. Propane, 1,3-butadiene and benzene. Operators use this analysis to verify analytical system accuracy.

Dilution Factor – A measure comparing the amount of a sample or standard and its diluent in a solution.

Flame Ionization Detector – Gas chromatographic detector for hydrocarbon analysis

Linearity Range – The acceptable range of response for the quantitation of results. The upper acceptance for this range is the highest calibration point.

Media Blank – A sample consisting of a clean sampling device (SUMMA[®] canister) filled with zero air used to assess the cleanliness of the sampling media.

Method Blank – A sample consisting of zero air used to assess potential contamination within an analytical system.

Method Detection Limit (MDL) – An analysis consisting of a series of known concentrations used to mathematically determine the threshold concentration for the minimum response - the minimum concentration of an analyte that can be measured and reported with a 99% confidence that the analyte concentration is greater than zero.

Percent Recovery – A calculation of a measured value compared to a theoretical value. The amount of a component recovered and detected from a known standard.

Precision – The measure of the reproducibility of a measured value

Response Factors (RF) – A measure that indicates a system's response to a known value, the ratio of the detector response to the amount of analyte in the calibration standard used for calibration in flame ionization detector and mass spectrometry.

Retention Time (RT) – The amount of time a specific compound resides in a chromatographic system before reaching the analytical detector.

Retention Time Verification Standard (RTS) – A sample with a blend of known compounds used to verify the location of those compounds in a chromatographic for the column and the time it takes for each compound to reach and pass through the detector.

Standard Deviation (STD) – A measure of the average distance of individual observations from the mean.

Relative Standard Deviation (RSD) – A measure of variability adjusted for the magnitude of observations involved.

Tentatively Identified Compounds (TICs) – Compounds detected in a sample that are not target compounds, internal standard, or surrogate compounds and are tentatively identified by mass spectral library searches, typically reported with estimated concentrations

7.0 Safety

All work performed must meet with the appropriate health and safety procedures as specified in the Houston Department of Health and Human Services Safety and Health Manual (May 2003).

7.1 Personal Protective Equipment

All City of Houston Bureau of Pollution Control and Prevention personnel, especially when performing field sampling, must have and wear all relevant personal protective equipment, including but not necessarily limited to eye protection, hard hat, Nomex[®] suits, steel-toed shoes, gloves, and hearing protection as specified by the HDHHS Safety and Health Manual.

7.2 Specific Safety Concerns or Requirements

Field Samplers and Operators can obtain health and safety information from the Material Safety Data Sheets (MSDSs) maintained by the laboratory. The sample sites and MAAML present potential electrical, physical, and chemical hazards such as the following specific concerns or hazards:

- Chemicals used: methanol, acetone, methylene chloride, hydrogen, zero air, helium.
- Compressed gas cylinders are often heavy and physically hard to handle. Secure all cylinders with either a strap or a chain to a sturdy, fixed structure. Never remove the safety cap on a cylinder while moving it. Move cylinders via a cylinder dolly only. Clearly mark empty and full cylinders. When attaching a regulator to a cylinder, use the appropriate CGA fitting. Check gas lines and fittings for leaks after cylinder or regulator replacement.
- Always unplug a heat traced line before maintenance and when disconnecting gas lines. Check for frayed or missing insulation before turning the power on.
- Check electrical systems periodically for loose connections, missing components, or frayed wires. Never use electrical tape to repair frayed wires or to join a spliced wire.
- If a circuit breaker throws, the Operator must turn off all instruments affiliated with that circuit before restoring power. Only then may the Operator turn on instruments sequentially to determine which instrument causes the breaker to throw.
- The thermal desorber and analytical instruments possess extreme heat and cold zones. The thermal desorber uses an electrically cooled trap that can reach a temperature of -15°C during sample collection while climbing to 315°C during desorption. The GC oven and FID may reach temperatures of up to 250°C. Avoid contact with the internal components of the instruments to avoid injury and burns. Cryogenic burn zones include the thermal desorber. Heated zones include the thermal desorber, GC oven, FID, and transfer lines.
- The enclosed space of the MAAML generates trip hazards in the form of electrical and sampling lines. Secure all such lines away from the main walkways or cover them with protective strips.
- The zero air and hydrogen gas generators produce gas on a continuous basis. Hydrogen gas is flammable and can accumulate in a confined area. Do not allow hydrogen gas to collect in one area, and always maintain adequate ventilation.

- A posted list of emergency phone numbers, contacts, and personal protective equipment including gloves, safety glasses, and a first aid kit must be available inside the MAAML and in the garage.

7.3 Materials Used

The following lists the primary materials used in this procedure possessing a serious or significant hazard rating. This does not include all materials used in the sampling effort or the sample matrices. Employees must review the information in the MSDS for each material before using it for the first time.

Material	Hazards	TCEQ Effects Screening Levels (ESLs) – long term	Signs or Symptoms of Exposure
Methanol	Flammable, Poison, Irritant	200 ppb	Slight irritant to the mucous membranes. Toxic effects exerted upon nervous system, particularly the optic nerve. Symptoms of overexposure may include headache, drowsiness and dizziness. Methanol is a defatting agent and may cause skin to become dry and cracked. Skin absorption can occur; symptoms may parallel inhalation exposure. Irritant to the eyes.
Methylene chloride	Carcinogen, Irritant	7.5 ppb	Causes irritation to respiratory tract, gastrointestinal tract. Strong narcotic effects with mental confusion, fatigue, nausea, vomiting and headache. Causes formation of CO in blood which affects cardio and central nervous system. Continued exposure may cause unconsciousness and death. Causes redness and pain on skin contact; liquid degrades the skin. Absorbable through the skin.
Acetone	Flammable, Irritant	250 ppb	Inhalation may irritate respiratory tract. May cause coughing, dizziness, and headache. Irritating due to defatting action on skin; causes redness, pain, drying and cracking of the skin. Long term exposure may produce central nervous system depressions, narcosis, and unconsciousness.

8.0 Equipment and Supplies

8.1 Field Sampling Equipment

- SUMMA® Canister
- Passive Air Sampling Kits
- Pressure Gauge
- Tedlar bag with polypropylene fittings
- Sampling box for generating a vacuum
- Appropriate Teflon and Tygon tubing
- Data sampling worksheet/Chain of custody form (Appendix A)
- Opaque trash bags (optional)

8.2 Markes Air Collection System

- Markes U-AirSV Air Server accessory unit
- Markes Unity Thermal Desorber

8.3 Agilent GC/FID/MS System

- Agilent Model 6890N network gas chromatograph with flame ionization detector (FID 210), dual EPA split/splitless inlets (112), a microfluid Dean's switch (888), pneumatics control module (309), LAN and 7683 interface
- Agilent Model 5975C Inert Mass Spectrometry Detector (MSD) performance turbo EI mainframe with G3397A ion gauge controller

9.0 Reagents and Standards

- GC Carrier Gas – GC grade helium (He) or equivalent.
- MS Instrument Performance Check Compound – 4-Bromofluorobenzene (BFB).
- MS Tuning Compound – Perfluorotributylamine (PFTBA).
- Calibration Standards – 100 ppbV of standards containing 51 compounds listed in Table 3.
- Analytical Internal Standards and Surrogates – 4-Bromofluorobenzene.
- System Purge Gas – UHP (ultra-high purity) helium.

10.0 Quality Control

Quality Control (QC) samples ensure that the data produced from a particular analytical source are of acceptable and consistent quality throughout the analytical procedure. Operators analyze QC samples to assess precision and accuracy. These include method blanks, media blanks, calibration samples and duplicates, laboratory control samples and duplicates, sample duplicates, surrogates, and internal standards. Table 1 lists a summary of the QC samples.

10.1 Method Blank

The method blank (MB), a control sample prepared using a well-characterized blank matrix (e.g. zero air), uses the same reagents used for sampling. As part of a QC batch, the method blank accompanies the samples through all steps of the analytical process. The MB monitors the level of contamination introduced to a batch of samples due to handling in the laboratory. Operators must process one MB per analytical batch, normally analyzed daily before beginning any sample analyses. The MB should not contain any confirmed analytes of interest > 2ppbc for FID, and >0.5 ppbV for MS. The sum of all target compounds must be < 20.0 ppbc. See Table 1 for a list of QC criteria.

Corrective Action for Method Blanks:

If a target analyte in the method blank exceeds the reporting limit, the Operator must reanalyze the method blank. If the reanalysis still fails the acceptance criteria, Field Samplers or Operators must re-sample all samples analyzed within the batch if possible. If re-sampling cannot occur, then the Operator must flag all associated samples with a “B” flag on the appropriate analyte of interest, with possible data invalidation after review. The Operator should add a narrative to the data to provide further documentation.

The following special situations may allow the reporting of qualified data without reanalysis, but will require a non-conformance memo (NCM).

- If no analyte exceeds the reporting limit in the samples associated with an unacceptable MB, the Operator may approve the data with qualifiers.
- If the analyte concentration in the samples exceeds a factor of 10 times the MB concentration, the Operator may approve the data with qualifiers.
- If the blank contamination remains less than the concentration present in the samples and registers less than 1/10th of the regulatory limit, the Operator may approve the data with qualifiers.

Any surrogates in the method blank must pass acceptance criteria. If the surrogates fail acceptance criteria, the Operator must review the data to determine if the MB has accurately demonstrated that the analysis shows no evidence of contamination, or if the MB matrix creates a matrix effect altering the surrogate recoveries.

10.2 Media Blank

Media blanks consist of clean sampling devices (SUMMA[®] canisters or Tedlar bags) filled with zero air used to assess the cleanliness of the sampling media. Operators should analyze the media blank at a frequency of 5%. Either a cleaned canister is pressurized to 30 psig or a 10-L Tedlar bag is filled to approximately 80% capacity with humidified zero air or nitrogen, then the media blank thus generated is analyzed via GC/FID/MS in the MAAML. The difference between the media blank and method blank should be less than 0.2 ppbv for any target compound.

Corrective Action for Method Blanks:

If the difference between the media blank and method blank for any target compound ranges higher than 0.2 ppbv, then all canisters need recleaning or the lot of Tedlar bags either flagged or removed from service.

10.3 Calibration Verification standard and Duplicate (CVS/CVSD)

Operators prepare the calibration verification standard (CVS) through obtaining the known concentrations of target compounds assess instrument accuracy. Operators analyze the CVS daily with an acceptable recovery criterion of 70-130% and routinely, i.e., weekly, analyze the CVS in duplicate (CVSD) to assess instrument precision from run to run. An RPD of $\leq 25\%$ constitutes the acceptable precision criterion. See Table 1 for a list of QC criteria.

Corrective Action for CVS/CVSD Recovery Failure:

If one or more analytes lie outside of the established control limits, check instrument performance and reanalyze the CVS or CVSD. If the reanalysis does not resolve the failures, replace the CVS standard and reanalyze. If still not resolved, contact the Technical Services Manager to assess whether any samples associated with the failing CVS require re-sampling. If Field Samplers and/or Operators cannot perform the re-sampling, flag the data with the appropriate flag.

The following special situations may allow the reporting of qualified data without reanalysis but will require a non-conformance memo (NCM).

- If Operators note a high recovery for the CVSD with no analytes detected in the sample, they may report the data with appropriate qualifiers.
- If low analyte concentrations result, Operators might find that the RPD calculations may reach a statistical limit of precision. In such cases, Operators may employ surrogate recoveries to provide acceptable evidence of accuracy control.
- In the case where all compounds of interest lie within control, but non-target compounds fall out of control, Operators may consider the CVS acceptable for reporting.

Corrective Action for CVS Precision Failure:

If established control limits for precision fail, check the instrument performance. If the RPD lies out of control, but both accuracy recoveries fall within acceptance criteria, prepare an NCM and qualify the data.

10.4 Surrogates

Surrogates, organic compounds similar in chemical nature and behavior to the target analytes but not normally found in environmental samples assist in addressing quality control issues. This procedure utilizes 4-bromofluorobenzene (BFB) as the surrogate for this procedure.

Operators spike samples in a batch with the surrogate to monitor the effects of both the matrix and the analytical process on accuracy. Operators evaluate surrogate spike recoveries by determining whether the concentration (measured as percent recovery) falls within the required recovery limits. Surrogate recoveries must lie within established control limits. Document any failure on the final data reports.

Corrective Action for Surrogates:

The surrogate must fall within established control limits for the CVS and method blank. Check all calculations to ensure generation of error-free results. Check the surrogate spiking solution for degradation, contamination, etc.

If Operators cannot discover the source for the failure of the surrogate spike, reanalyze the QC sample. If reanalysis does not confirm the original analysis, and lies within acceptance criteria, then the problem laid within the analyst's control with the Operator reporting only the reanalyzed data. If the surrogate recovery still fails, reanalyze batch if samples are available.

If the surrogate fails acceptance criteria in a field sample, reanalyze the field sample if possible to check for matrix interference, i.e. humidity, interfering compounds, or interference from a prior analysis. Document the failure and note it on the final data report.

10.5 Internal Standards

Operators add internal standards to each analytical standard, ambient sample, and blank sample for analysis via the mass spectrometer detector. The acceptance criteria for each internal standard must fall within $\pm 50\%$ recovery of the internal standard area from the calibration verification standard (CVS). The acceptance criteria for each internal standard's retention time in every analysis must lie within ± 20 seconds of the internal standard retention time from the continuing calibration standard.

Corrective Action for Internal Standards:

If internal standard fall outside acceptance criteria, check instrument performance and the internal standard spiking standard for degradation. If unresolved, search for possible matrix effects, including coelutions, interferences, excess moisture, et al. Reanalyze the sample, and if still outside of control limits, issue an NCM if Operators suspect interference.

10.6 Retention Time Verification Standard (RTS)

The RTS, composed of targeted compounds of FID spiked near the mid-point concentration of the calibration range, assesses the qualitative ability of the system to identify peaks in a chromatogram with FID detector. Operators should analyze an RTS after installation of a new column and then as needed based on performance. Failure of the system to identify these RTS compounds correctly will require instrument optimization by the operator.

11.0 Calibration and Standardization

11.1 Initial Calibration Verification and Curve Fits

11.1.1 GC/FID

An initial calibration curve (ICAL-FID) consists of five concentration levels analyzed to determine the working linear range of the analytical system for each compound. The concentration of the low point should equal or fall below the reporting limit.

The calibration curve correlation coefficient (r) must lie within ≥ 0.995 or an RSD with RFs $< 20\%$. If any curve fits fail the acceptance criteria, check the system performance, and repeat analysis of outlying points.

11.1.2 GC/MS

An initial calibration curve (ICAL-MS) consists of five concentration levels (1, 5, 10, 20, and 40 ppbv) analyzed to determine the working linear range of the analytical system for each compound. The concentration of the low point should lie at or below the reporting limit.

The calibration curve correlation coefficient (r) must lie within ≥ 0.995 or RSD with RFs $< 30\%$, with two exceptions of $< 40\%$. If any curve fits fail the acceptance criteria, check the system performance, and repeat analysis of outlying points.

Initial Calibration Verification:

The initial calibration verification (ICV) represents a secondary source standard containing target analytes, analyzed immediately after the initial calibration. For each analyte, Operators calculate a percent recovery using the average response factor with the acceptance criteria set for guidance at $\pm 35\%$. If the ICV fails acceptance criteria, reanalyze ICV and check instrument performance. If the ICV still fails, check ICAL analyses for problems or statistical anomalies.

11.2 Daily Calibration Verification (CVS)

Every 24 hours of operation, Operators must analyze a calibration verification standard (CVS) to assess instrument performance and to verify the response factors generated from the ICAL. The CVS represents a standard containing known amounts of target analytes routinely spiked in the mid-range of the calibration linearity range. The percent difference (%D) is calculated between the CVS RF from the ICAL average RF. In general, the %D must be within $\pm 30\%$.

Calibration Verification Standard Failure:

As long as less than 10% of all analytes in the CVS fail the acceptance criteria, continue the analysis with the failing compounds flagged appropriately. If more than 10% of all analytes fail the acceptance criteria, check instrument performance and reanalyze the CVS. If the CVS still fails, Operators must perform corrective maintenance.

12.0 Procedure

12.1 Method Summary – Canister Sampling

Field Samplers and Operators sample ambient air in a specially passivated SUMMA[®] canister. There are two types of passive sampling techniques: grab sampling and integrated sampling. For grab sampling, a pre-evacuated SUMMA[®] canister collects an ambient air in a very short time interval. For integrated sampling, a critical orifice designed to regulate the flow rate and duration (usually 30 min) on a pre-evacuated SUMMA[®] canister extends the collection time for an ambient air sample. After collecting the air sample and recording all necessary information on the Canister Data Sheet and Chain-of-Custody (COC) forms, the Field Sampler or Operator delivers the canister to the MAAML. Upon receipt at the MAAML, the Operator stores the canister until analysis. Prior to analysis, the Operator pressurizes samples at sub-atmospheric pressure to at least twice the collected volume.

The Operator analyzes for air toxics in the canister using the Markes Thermal Desorber and Agilent GC/FID/MS system. The instruments consist of a gas chromatograph equipped with flame ionization and mass spectrometry detectors. The system uses a Markes U-AIRSV to collect air samples or induce the standard samples.

The system draws a specified volume of sample air (500 cc for ambient samples) from the canister into the Markes Thermal Desorber. A Nafion[®] based drying membrane removes excess moisture in the sample. An electrically cooled cold trap in the thermal desorber collects the dry sample. The cold trap concentrates the sample to achieve high sensitivity for very low concentrations of air toxics. Heating the preconcentrator rapidly thermally desorbs the sample, and then a reversal of the carrier gas' flow backflushes the VOCs into the gas chromatograph. Due to the wide boiling point range of the VOCs, the GC has dual columns: PLOT column for light compounds and BP1 column for heavier compounds. The Dean's switch allows hydrocarbons with C₁ through C₃ that elute from the BP1 column first to move through the PLOT column for detection by the flame ionization detector. The high boiling point materials from C₄ through C₁₀ eluted late from the BP-1 column get detected using mass spectrometry. Figure 1 depicts an overview of the sample path for the system. Figure 2 shows the GC/MS and Unity cycles. Figure 3 shows the elution sequence of targeted compounds for PLOT column and BP1 Column.

12.2 Method Summary – Tedlar Bag Sampling

Tedlar bag sampling allows for the collection of a representative grab (direct) or an integrated (indirect) sample of a gaseous media for analysis. Field Samplers and Operators perform grab sampling via directly connecting in series a sampling pump and a Tedlar bag with appropriate tubing. The Tedlar bag collection system allows for integrated sampling and consists of the following:

- A Tedlar bag complete with necessary fittings (typically polypropylene)
- A box for creating a vacuum
- A sampling pump to create the necessary vacuum
- An appropriate Teflon and Tygon tubing

The Field Sampler or Operator places the Tedlar bag into a vacuum box (Appendix B) and puts the Teflon tubing over the polypropylene fitting for integrated (indirect) sampling. The Teflon tubing represents the path through which the gaseous media will travel. Then Field Sampler or Operator attaches the pump to the Tygon tubing, part of the vacuum fitting on the vacuum box. The pump evacuates the air in the vacuum box, creating a pressure differential causing the sample to be drawn into the bag. The sample drawn into the Tedlar bag never flows through the pump. The Field Sampler or Operator sets the flow rate for the pump prior to sampling with the usual flow rate for bag sampling at 0.5 liters/minute (l/min).

For grab (direct) sampling, the Field Sampler or Operator connects the outlet tubing from the sampling pump to the polypropylene fitting on the Tedlar bag. The Field Sampler or Operator then opens the valve on the Tedlar bag, turns on the sampling pump, and collects the ambient air sample in the Tedlar bag.

The Operator analyzes for air toxics in the Tedlar bag using the Markes Thermal Desorber and Agilent GC/FID/MS system. The instruments consist of a gas chromatograph equipped with flame ionization and mass spectrometry detectors. The system uses a Markes U-AIRSV to collect air samples or induce the standard samples.

The system draws a specified volume of sample air (500 cc for ambient samples) from the canister into the Markes Thermal Desorber. A Nafion[®] based drying membrane removes excess moisture in the sample. An electrically cooled cold trap in the thermal desorber collects the dry sample. The cold trap concentrates the sample to achieve high sensitivity for very low concentrations of air toxics. Heating the preconcentrator rapidly thermally desorbs the sample, and then a reversal of the carrier gas' flow backflushes the VOCs into the gas chromatograph. Due to the wide boiling point range of the VOCs, the GC has dual columns: PLOT column for light compounds and BP1 column for heavier compounds. The Dean's switch allows hydrocarbons with C₁ through C₃ that elute from the BP1 column first to move through the PLOT column for detection by the flame ionization detector. The high boiling point materials from C₄ through C₁₀ eluted late from the BP-1 column get detected using mass spectrometry. Figure 1 depicts an overview of the sample path for the system. Figure 2 shows the GC/MS and Unity cycles. Figure 3 shows the elution sequence of targeted compounds for PLOT column and BP1 Column.

12.3 Field Sampling

12.3.1 Field Sampling Preparations

Determine the extent of the sampling effort, the sampling methods of choice and the types and amounts of equipment and supplies needed.

Obtain and organize the necessary sampling and monitoring equipment.

Decontaminate or pre-clean equipment, and ensure that its readiness for sampling.

Prepare scheduling and coordinate with staff, client, and the department, if appropriate.

Perform a general site survey prior to entry, as per the site specific Health and Safety Plan.

12.3.2 Canister Cleaning and Certifying

Use only pre-cleaned SUMMA[®] canisters for sampling ambient air. The typical cleaning process includes the following steps:

Connect the canisters to the cleaning system, release any pressure within any of them, and evacuate them. A reduced pressure of 23-25 in Hg is sufficient for general cleaning.

After the canisters have been under vacuum for approximately 1 hour, pressurize them with nitrogen to 5 psig if heated during cleaning, or 30 psig if not. Pressurization will dilute the contaminants and the water vapor will hydrolyze them. When the system has equilibrated at the designated pressure, proceed to step c (heating) or step d (no heat)

Heat the pressurized canisters to the appropriate temperature, i.e., 90°C for all canisters fitted with a gauge or 250°C for all canisters without a gauge.

Allow the canisters to equilibrate for at least 1 hour. Evacuate the canisters to remove the impurities and then allow them to equilibrate for 1 hour. Repeat the steps b – c as necessary.

The Operator determines the number of cycles required for canister cleaning by the VOC concentrations of the sample remaining in the canister and the ease of cleaning each canister. Without heat, the Operator may need to increase the number of cycles required to clean the canisters.

To certify a canister as clean, pressurize the cleaned canister to 30 psig with humidified certified ultra-high purity air or nitrogen, and then analyze the canister sample using GC/FID/MS in the MAAML. The difference between the media blank and method blank should show less than 0.2 ppbv for any target compound.

12.3.3 Field Sampling - Canister

Field Samplers and/or Operators must check canisters before sampling to include checking that the canister number on the Canister Sampling Data Sheet and Chain-of-Custody form (Appendix A) matches the number on the canister. In addition, they must check the canister pressure using a vacuum gauge with an accuracy of 0.2 inches Hg and record the reading as pre-sampling pressure. Field Samplers and/or Operators must not use a canister for differences between pre-sampling pressure and upon receipt pressure greater than 2 inches Hg.

To take a grab sample, remove the brass cap from the canister inlet. Slightly open the blue valve located downstream from the canister inlet. Close the valve when the vacuum gauge reading approaches 7 inches Hg. Record the gauge reading as post-sample pressured. Replace the brass cap on the canister inlet and tighten.

To take a time-integrated sample, remove the brass cap from the canister inlet. Fix a critical orifice designed to regulate the flow rate and duration (usually 30-minute sample) to the canister inlet. Open the blue valve. Close the valve when the vacuum gauge reading approaches 7 inches Hg. Record the gauge reading as post-sample pressured. Disassemble the critical orifice kit. Replace the brass cap on the canister inlet and tighten.

12.3.4 Field Sampling – Tedlar Bag

To take a time-integrated sample, the Field Sampler or Operator should follow the steps below:

Remove the Tedlar bag from the carton.

Insert valve stem into Teflon tubing running through vacuum box (Figure 1 - Appendix).

Place the Tedlar bag in the vacuum box. Seal the vacuum box by applying pressure to the top and bottom (ensure that the O-ring is in place and unobstructed).

Connect the sampling pump to the evacuation tube.

Connect the intake tube to desired source or place intake tube into media of concern.

Turn on the sampling pump.

Allow the bag to fill (visual observation and sound of laboring pump).

Turn off the sampling pump and remove the evacuation tube from the pump.

Remove bag and pull the valve stem out.

Lock the valve stem.

Label the bag using either a tag or sticker placed on the edge of the bag. Do ***not*** write on the bag itself.

Place Tedlar bag in clean cooler or opaque trash bag to retard photo-degradation.

To take a grab sample, the Field Sampler or Operator should follow the steps below:

Remove the Tedlar bag from the carton.

Insert the valve stem into Teflon tubing.

Connect the Teflon tubing to the exhaust port on the sampling pump.

Connect the intake tube to the desired source or place the intake tube into the media of concern.

Turn on the sampling pump.

Allow the bag to fill (visual observation and sound of laboring pump).

Turn off the sampling pump and remove the evacuation tube from the pump.

Lock the valve stem.

Remove bag and pull the valve stem out.

Label the bag using either a tag or sticker placed on the edge of the bag. Do **not** write on the bag itself.

Place the Tedlar bag in a clean cooler or opaque trash bag to prevent photo-degradation.

Upon completion of sample collection, transfer all collected samples to the laboratory for analysis. Operators must conduct Tedlar bag sample analyses within **48 hours** of sample receipt, as after this time compounds may escape or become degraded.

When transferring Tedlar bags, a chain of custody form must accompany the samples.

Note: Personnel should note that some of the chemicals of concern will degrade within a few hours of sampling. A study conducted by Posner and Woodfin (1986) showed that over a 4 to 6 hour period, benzene losses approached 5%.

For the time prior to analysis, Field Samplers and/or Operators may store samples in a clean cooler or an opaque trash bag with a trip blank (a Tedlar bag filled with “zero air”) and the chain of custody form(s).

12.4 Sample Receipt and Preparation

Record all sample information such as sample type, sample location, weather conditions, both sample date and time, name of sampler etc. on the Canister Sampling Data Sheet and Chain-of-Custody Form. Deliver the sample to the MAAML.

When the sampler relinquishes the canister and an Operator receives it, the Operator records the data and time of the custody change and the initials of each individual involved on the Chain-of-Custody Form. Store the canister in the MAAML until analysis. Operators must analyze the sample within 30 days after sampling.

Prior to analysis, an Operator pressurizes all samples with gauge readings at sub-atmospheric pressures to as least twice the collected volume. Check the canister pressure using a gauge with an accuracy of 0.2 inches Hg or 0.1 psi and record the reading as pre-dilution pressure. Operators should report relevant observations to the supervisor or quality control officer if the difference between pre-dilution pressure and post-sampling pressure ranges greater than 2.0 inches Hg.

Pressurize the canister to about 15 psi using ultra-high purity air or nitrogen. Record the gauge reading as post-dilution pressure. Calculate the dilution factor:

$$DF = \frac{P_3 + 14.7}{ABS(P_2 - P_1)/2.036}$$

where P1 inches Hg = pre-sampling pressure
 P2 inches Hg = pre-dilution pressure
 P3 psig = post-dilution pressure

12.5 Instrument Preparation

12.5.1 GC/FID

Each new column used for this method must undergo a 72-hour retention time study. Operators must calculate retention time windows (RTW) for each analyte on each GC column. Operators perform three injections of the appropriate standard throughout the course of a 72-hour period with the standard deviation of the three absolute retention times calculated for each single component. In the case where the standard deviation for a particular compound equals zero or less than 1.8 seconds, Operators will use as the RTW the default of 1.8 seconds per SW-846.

The retention time of each analyte, as established by the daily calibration check standard, plus or minus three times the standard deviation of the absolute retention times of the 72-hour RTW study, defines the daily RTW. Operators use six times the standard deviation for instruments with electronic pressure control (EPC). Retention time windows greater than 1.5% indicate a problem with the system with Operators required to take corrective action.

Check for successful ignition of the FID. Condensation on a metal object held above the FID chimney will indicate the presence of a flame. If the instrumentation did not successfully ignite the FID, the instrument's auto-igniter or a coil lighter can ensure proper ignition.

Verify communication to the computer, and create an analytical sequence in the ChemStation software, taking care to use the current methods and correct report formats. Include all QC and samples for be analyzed.

Download the sequence to the data interface or data logger. Ensure proper downloading of the next sample for analysis.

12.5.2 GC/MS

An Operator may use an autotune as a diagnostic tool in troubleshooting the mass spectrometer (MS). It also establishes the optimal voltages in the ion source. Operators must perform an autotune after major maintenance to the mass spectrometer with the settings compared to the last autotune performed. Significant differences between the new and previous autotune may indicate a problem with the mass spectrometer. Upon completion of the autotune, the Operator completes a maximum sensitivity autotune and stores it on the computer using as the name the date performed, e.g., Jan0107.u. The Operator then reviews the resulting tune report and compares it to previous reports. Significant differences may require recalibration of the GC/MS.

The Operator evaluates the filament current by ramping up the repeller using different filament current settings. The curves thus generated represent an acceptable filament current when good separation of the peak maxima occurs for all three masses (69,219, 502) from the tuning compound, PFTBA.

The Operator may adjust the sensitivity of the mass spectrometer by increasing the voltage on the electron multiplier. Operators assess the need to perform this task by examining the area of the internal standards and comparing them with those generated during the last detection limit study. If the areas represent less than 50% of those found in the detection limit study, the Operator may increase the voltage to the multiplier to correct for the loss of sensitivity.

Operators perform a daily check of the instrument tune by evaluating the 4-bromofluorobenzene (BFB) from the first QC sample that passes its acceptance criteria at the beginning of the sequence. Then, the Operator averages the spectrum of the full BFB and subtracts a background scan before evaluation. The Operator selects the header "tuner" option under which the Operator picks the task of "evaluate BFB to screen". The resulting report contains the tune acceptance criteria that the tune must meet in order to analyze samples. See Table 2.

Verify communication to the computer, and create an analytical sequence in the ChemStation software, taking care to use the current methods and correct report formats. Include all QC and samples for analyzed.

12.5.3 Instrument Settings

The table below shows the Markes U-AIRSV and Agilent GC/MS/FID settings for use in the ozone precursor analysis:

GC Function Key	GC Parameter	Default Method
Oven Programming	Temp 1	45 °C
	Time 1	15.0 min
	Rate 1	6.5 °C/min
	Temp 2	170 °C
	Time 2	0.0 min
	Rate 2	15.0 °C/min
	Temp 3	200 °C
	Time 3	6.0 min
	Rate 3	END
TD Programming (ambient sample)	Sample rate	12.5 mL/min
	Sample time	40.0 min for ambient sample
	Trap temp	-15 °C
	Purge	2.0 min
	Purge rate	10 mL/min
	Desorb time	3/min
	Desorb temp	325 °C

12.5.4 Sequences

A sequence file represents a table of instructions used by the Markes U-AIRSV or GC/FID/MS system to control collection, analysis, and interpretation parameters. For routine analysis, the Operator must create sequence files for both the Markes U-AIRSV and GC/FID/MS systems separately, and then correlate these files to maintain sample and data integrity. The instrumentation then adds an internal standard to an ambient (calibration, blank, etc) sample before the sample desorption into the GC.

Each row in the sequence for Markes U-AIRSV (Figure 4) corresponds to one set of instructions for the collected sample, including the sample number, the sample type, the instrument method (Figure 5) used for the sample collection, and sample channel.

Sample Type	Channel	Method Name
Blank	3	Airserver_method_blank(500c).mth
45 compounds standard	1	Airserver_50cc(10ppb_mod).mth
16 compounds standard	5	Airserver_50cc(10ppb_mod).mth
Internal standard	2	Airserver_Intenalstand(IS_5ppb).mth
Ambient	4	Airserver_500c(sample_mod).mth
Canister or bag	6, 7 & 8	Airserver_500c(sample_mod).mth for ambient sample

Each row in the sequence for GC/FID/MS (Figure 6) corresponds to one set of instructions for a sample for analysis to include sample type, process method used for interpretation of the raw data, and the filename for the raw data files and analysis result files.

12.5.5 Process Methods

The analytical systems' process methods contain the parameters that define the type of sample (canister or bag sample, standard, or blank) collected and the basis for raw data interpretation. Since the analytical system in the MAAML employs a dual column sampler with a separate collection instrument, the system requires three methods. EnviroQuant ChemStation and the Markes U-AIRSV use these methods to take canister samples or standard samples, define integration principles, identify peaks, and calculate compound concentration from peak area.

12.5.6 Data File Nomenclature

During analysis, the software continually records analytical information in a raw file (*.raw). This file contains information such as sample acquisition time, FID response, and MS response. Upon completion of the sample run, the software closes the raw file. ChemStation can then use the information to process the data into result (*.rst), or text, (*.txt) files. ChemStation uses the data stored in the raw files to analyze information and create results, or text files. The result files yield interpreted information such as component name, concentration, and elution time. The text files represent the same information in an easily transferable electronic format, e.g. ASCII or Excel.

Filenames have two parts: the file extension that defines the presentation of the information and the root file name. The root file name gives each analysis a unique identifier that provides information as to its origin. The name below reflects the format for the canister data file.

Canister####_MMDDHH

where #### = the canister number. MMDDHH = the analyzed date.

12.6 Sample Analysis

Create a short sequence in both the Markes and Agilent systems. Operators reserve the first three top samples of each short sequence for the method blank, a calibration, and a calibration duplicate. Operators use appropriate sample methods for the various types of samples potentially comprising an analytical sequence.

Attach the appropriate QC standards to the sample ports on the Markes air server. Open all canister or cylinder valves and check all pressure gauges.

Start Markes and Agilent systems using the sequences. Close satellite standard containers or cylinder after calibration sample desorption.

After the calibration verifications and method blanks are completed, run the "qedit" program in ChemStation to ensure correct identification of all relevant peaks and the drawing of the baselines. Save any changes made and regenerate the summary report. Then quantify the calibration and blanks samples.

If QC meets all acceptance criteria, MAAML will analyze ambient samples, canister samples or bag samples. Operators must analyze another blank sample and calibration after every 23 ambient, canister or bag samples.

Prepare a final analysis report for each canister sample or Tedlar bag sample (Appendix B). The analysis report includes such things as analysis results and QA & QC samples, including calibration samples, duplicate calibration samples, blank samples, etc.

13.0 Data Analysis, Qualifiers, and Calculations

13.1 Data Analysis

A trained analyst may perform manual changes in the instrument data. The mathematical algorithms used to integrate the sample peaks automatically may at times not fully and accurately integrate the peaks. For such occurrences, Operators may perform manual integrations to modify those misshapen integrations into an optimized interpretation. Operators must save the altered data with a different file extension to indicate the performance of a manual integration. For mass spectrometry data integrations using ChemStation, Operators must have the audit trail function turned on at all times. Operators must transfer all data to the AIM server for storage and immediate public display. Operators must redistribute through the AIM server for storage all data in which they performed manual integrations.

13.2 Qualifiers

While reviewing the data, the operators and reviewer may flag any data that does not comply with the appropriate quality specifications with the appropriate qualifiers. The following flags that include, but are not limited to, may apply to the data.

Flag	Definition
B	Analyte detected in method blank above 0.5 ppbv and analysis result is <10 times the value in the method blank
I	Interference or co-elution suspected
NA	Not analyzed/Not available
C	Daily calibration sample does not meet the criteria
D	Duplicate calibration sample does not meet the criteria
ND (U)	Not detected at the specified reporting limit
Q	Result does not meet specification
U	Result less than sample specific method detection limit

13.3 Calculations

Relative Percent Difference (RPD):

$$RPD = \frac{|x_1 - x_2|}{\left(\frac{x_1 + x_2}{2}\right)} * 100$$

where:

x_1 = analytical % recovery

x_2 = replicate % recovery

Percent Recovery:

$$\%R = \frac{[MeasuredConcentration]}{[TheoreticalConcentration]} * 100$$

Response Factor for MS:

$$RF = \frac{(A_x C_{is})}{(A_{is} C_x)}$$

where:

A_x = area of the characteristic ion for the compound being measured

A_{is} = area of the characteristic ion for the specific internal standard

C_{is} = concentration of the specific internal standard ($\mu\text{g/mL}$)

C_x = concentration of the compound being measured ($\mu\text{g/mL}$)

Average Response Factor for MS:

$$\overline{RF} = \frac{\sum (RF_1 + RF_2 + \dots RF_n)}{n}$$

where:

RF_1 = response factor for first calibration point of a compound

RF_2 = response factor for second calibration point of a compound

RF_n = response factor for last calibration point of a compound

n = total number of calibration points

Standard Deviation:

$$s = \sqrt{\frac{\sum_{i=1}^n (x_i - \bar{x})^2}{n - 1}}$$

where:

n = total number of measurements in the set

x = individual measurements

\bar{x} = measured mean for the set

Canister Dilution Factor:

$$DF = \frac{P_3 + 14.7}{ABS(P_2 - P_1)/2.036}$$

where P1 inches Hg = pre-sampling pressure
 P2 inches Hg = pre-dilution pressure
 P3 psig = post-dilution pressure

Concentration of Analyte in a Sample Using Average Response Factor for MS:

$$Concentration = \frac{(A_x)(C_{is})(DF)}{(A_{is})RF}$$

where:

A_x = area counts of characteristic ion for compound being measured
 C_{is} = concentration of internal standard injected (µg/L)
 A_{is} = area counts of characteristic ion for the internal standard.

Calibration Factor (CF) for FID:

$$CF = \frac{PeakArea}{Concentration}$$

Sample Concentration for FID:

$$PeakConcentration = \frac{PeakArea}{CalibrationFactor}$$

Method Detection Limit:

$$MDL = (S)(t)$$

where:

S = standard deviation of the replicate analyses
 t = students' t value for 99% confidence level and a standard deviation estimate with n-1 degrees of freedom

14.0 Method Performance

14.1 Training

- The analyst must complete the laboratory safety orientation training that includes, but is not limited to, chemicals, PPE requirements, and electrical safety.
- The analyst must read and understand this SOP.
- The analyst must have a completed training record approved by the technical services chief.

14.2 Responsibilities

14.2.1 Operator

The operator shall:

Daily:

- Verify proper system operating status,
- Verify the operation of the modem and data logger,
- Ensure that the analytical systems are functioning and collecting data,
- Review the daily calibration verification standard and method blank results,
- Check the peak identification, integration, and general chromatography of all samples collected,
- Optimize the methods if necessary,
- Verify BFB tuning requirements,
- Update electronic and written logbooks,

Weekly:

- Analyze the second source laboratory control standard (LCS) in duplicate (LCSD),

Bi-weekly

- Review and update sequence files,
- Check gas generation stations

Monthly:

- Verify all data archival,
- Routine data backup to CD/R/RW,
- Perform any computer or instrument maintenance as necessary.

14.2.2 Lab/Technical Manager

The lab/technical manager shall:

- Certify that the project specification are being met,
- Ensure that each operator has been properly trained in its use and has the required experience to perform this procedure,
- Ensure that this training/experience is documented,
- Periodically review all logs and logbooks documenting this review.

15.0 Waste Management

Field Samplers and Operators must dispose of all waste generated during the performance of this procedure in accordance with the City of Houston Waste Management Plan. Contact the waste management coordinator if additional information is required.

Laboratory personnel assigned to perform hazardous waste disposal procedures must have a working knowledge of the established procedures and practices of the City of Houston. They must have training on the hazardous waste disposal practices upon initial assignment to these tasks, followed by annual refresher training.

16.0 References, Deviations and Clarifications

16.1 References

- TCEQ. Revision 12, May 2003. PAMS Network Quality Assurance Project Plan for Monitoring Texas. TCEQ. Austin, TX
- TCEQ, May 2005. Standard Operating Procedure, Perkin-Elmer Auto Gas Chromatography for VOC Ozone Precursor Analysis
- EPA, October 2003. Compendium Method TO15, "The Determination of Volatile Organic Compounds (VOCs) in Air Collected in SUMMA[®] Canisters and Analyzed by Gas Chromatography/Mass Spectrometry (GC/MS)"
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Posner, J.C. and W.J. Woodfin, Sampling with Gas Bags 1: Losses of Analyte with Time, Applied Industrial Hygiene 4, 163-168, 1986.

Roy F. Weston, Inc., Weston Instrument Manual, Volume I, 1987.

U.S. EPA, Compendium of Methods for Determination of Toxic Organic Compounds in Ambient Air, EPA 600/4-84/76, December 1984.

17.0 Tables, Figures and Appendices

Table 1: Summary of Calibration and QC Analyses

Table 2: BFB Key Ions and Abundance Criteria

Table 3: Analyte Lists and Quality Control

Figure 1: Sample Path

Figure 2: GS/MS and Unity2 cycle chart

Figure 3: Elution sequences for FID and MS

Figure 4: Control Sequence for Unity

Figure 5: Control Sequence for GC/FID/MS

Appendix A:

Appendix B:

Appendix C:

Appendix D:

Table 1. Summary of Calibration and QC Analyses

Calibration & QC Analyses	Description	Frequency	Acceptance Criteria	Corrective Action
Initial Calibration (ICAL)	FID: 5-point calibration MS: 5-point calibration	Minimum annually or when calibration verification fails to meet acceptance criteria	FID: a calibration curve correlation coefficient (r) ≥ 0.995 or an RSD of RFs $< 20\%$. MSD: a calibration curve correlation coefficient (r) ≥ 0.995 or an RSD of RFs $< 30\%$, with two exceptions of $< 40\%$.	1. Reanalyze concentration not meeting criteria 2. Troubleshoot instrument
Demonstration of Capability (DOC)	Quadruplicate analysis of second source standard	1. Initial method setup 2. For each new analyst prior to analysis of any samples	Mean Accuracy: % Recovery $\pm 35\%$	1. Verify calibration with second source standard 2. Troubleshoot instrument.
Calibration Verification Standard (CVS)	Standard for assessment of instrument accuracy containing analytes of interest	Daily	70%-130% recovery	1. Repeat CVS 2. Troubleshoot 3. Recalibrate
Method Blank (MB)	Zero Air used to monitor the level of contamination introduced to a batch of	Daily	FID: 1. Target compound concentrations ≤ 2.0 ppbc 2. TNMHC values ≤ 20.0	1. Reanalyze MB 2. If not resolved, reanalyze all samples 3. If reanalysis not possible, flag all

	samples as a result of handling in the laboratory		ppbc MS: Target compounds \leq 0.5 ppbV	data <ul style="list-style-type: none"> • If no analyte > RL in samples, data may be reported without flags • If analyte concentration in sample is > 10 times the MB concentration, may be reported with qualifiers 4. Troubleshoot instrument.
Media Blank	A canister with humidified zero air or nitrogen.	Every 20 canisters	Difference between the media blank and method blank for any target < 0.2 ppbv	Reclean all canisters.
Calibration Verification Standard Duplicate (CVSD) for Precision	Standard containing analytes of interest analyzed in duplicate	Weekly	Precision: <25%	1. Reanalyze CVSD 2. Reprep CVS standard and analyze 3. Troubleshoot instrument.
Retention Time Standard (RTS)	Standard containing target compounds identified by FID.	Initial study after installation of a new column and then bi-weekly or as needed based on performance	Retention time window is set at plus or minus three times the standard deviation of the absolute retention times for the 72-hour study	1. Identify and correct source of problem. 2. Repeat study.

BFB Tuning Check	Evaluation of 4-bromofluorobenzene (BFB) peak in the calibration verification.	At the beginning of each analytical sequence	Must meet ion abundance criteria listed in Table 2.	<ol style="list-style-type: none"> 1. Evaluate BFB in method blank 2. Re-tune and reanalyze BFB 3. Troubleshoot, retune if necessary.
Internal Standards	Three internal standard added to each sample, standard, and blank	All samples, standards, and blanks	Measured area must be $\pm 50\%$ of internal standard area from the calibration verification standard (CVS)	<ol style="list-style-type: none"> 1. Reanalyze sample if out of specification 2. Identify and correct problem 3. Recalibrate
Analytical Surrogate	One surrogate compounds are added to each sample, standard, and blank	All samples, standards, and blanks	Accuracy: 50%-150% recovery	<ol style="list-style-type: none"> 1. Reanalyze sample for matrix effect evaluation 2. If matrix specific, flag data 3. Troubleshoot instrument

Table 2. BFB Key Ions and Abundance Criteria

Mass	Ion Abundance Criteria
50	8.0 to 40% of mass 95
75	30 to 66% of mass 95
95	Base peak, 100% relative abundance
96	5.0 to 9.0% of mass 95
173	<2% of mass 174
174	50 to 120% of mass 95
175	4.0 to 9.0% of mass 174
176	93 to 101% of mass 174
177	5.0 to 9.0% of mass 176

Table 3. Standard Analyte Lists

Name	CAS No.	MDL (ppbv)*
Ethane	74-84-0	0.1
Ethylene	74-85-1	0.1
Propane	74-98-6	0.1
Dichlorodifluoromethane	75-71-8	0.8
Propylene	115-07-1	0.1
Ccetylene	74-86-2	0.1
Methyl chloride	74-87-3	0.3
1,2-Dichlorotetrafluo...	76-14-2	0.4
Vinyl Chloride	75-01-4	0.2
1,3-Butadiene	106-99-0	0.4
n-Butane	106-97-8	0.2
Bromomethane	74-83-9	0.2
Ethyl Chloride	75-00-3	0.3
Trichlorofluoromethane	75-69-4	0.1
n-Pentane	109-66-0	0.1
1,1-Dichloroethylene	75-35-4	0.1
Methylene Chloride	75-09-2	0.3
1,1,2-Trichlorotrifluo...	76-13-1	0.3
1,1-Dichloroethane	75-34-3	0.2
2-Methylpentane	107-83-5	0.1
1-Hexene	592-41-6	0.1

Cis-1,2-Dichloroethylene	156-59-2	0.3
Hexane	110-54-3	0.1
Chloroform	67-66-3	0.5
1,2-Dichloroethane	107-06-2	0.4
1,1,1-Trichloroethane	71-55-6	0.6
Benzene	71-43-2	0.2
Carbon Tetrachloride	56-23-5	0.8
1,2-Dichloropropane	78-87-5	0.5
Trichloroethylene	79-01-6	0.2
Cis-1,3-Dichloropropene	10061-01-5	0.4
Trans-1,3-Dichloropropene	10061-02-6	0.2
1,1,2-Trichloroethane	79-00-5	0.3
Toluene	108-88-3	0.2
1,2-Dibromoethane	106-93-4	0.2
Tetrachloroethylene	127-18-4	0.3
1,1,1,2-Tetrachloroethane	630-20-6	0.2
Chlorobenzene	108-90-7	0.1
Ethylbenzene	100-41-4	0.1
m/p-Xylene	108-38-3 & 106-42-3	0.3
Styrene	100-42-5	0.1
o-Xylene	95-47-6	0.1
1,1,2,2-Tetrachloroethane	79-34-5	0.3
Cumene	98-82-8	0.2
1,3,5-Trimethylbenzene	108-67-8	0.1
1,2,4-Trimethylbenzene	95-63-6	0.1
1,3-Dichlorobenzene	541-73-1	0.1
1,4-Dichlorobenzene	106-46-7	0.1
1,2-Dichlorobenzene	95-50-1	0.2
1,2,4-Trichlorobenzene	120-82-1	0.4
Hexachloro-1,3-Butadiene	87-68-3	0.3

* The values of MDL are based on 500 cc undiluted sample.

Surrogate

- Bromofluorobenzene (BFB)

Internal Standards

- Bromochloromethane
- 1,4-Difluorobenzene
- Chlorobenzene-d5

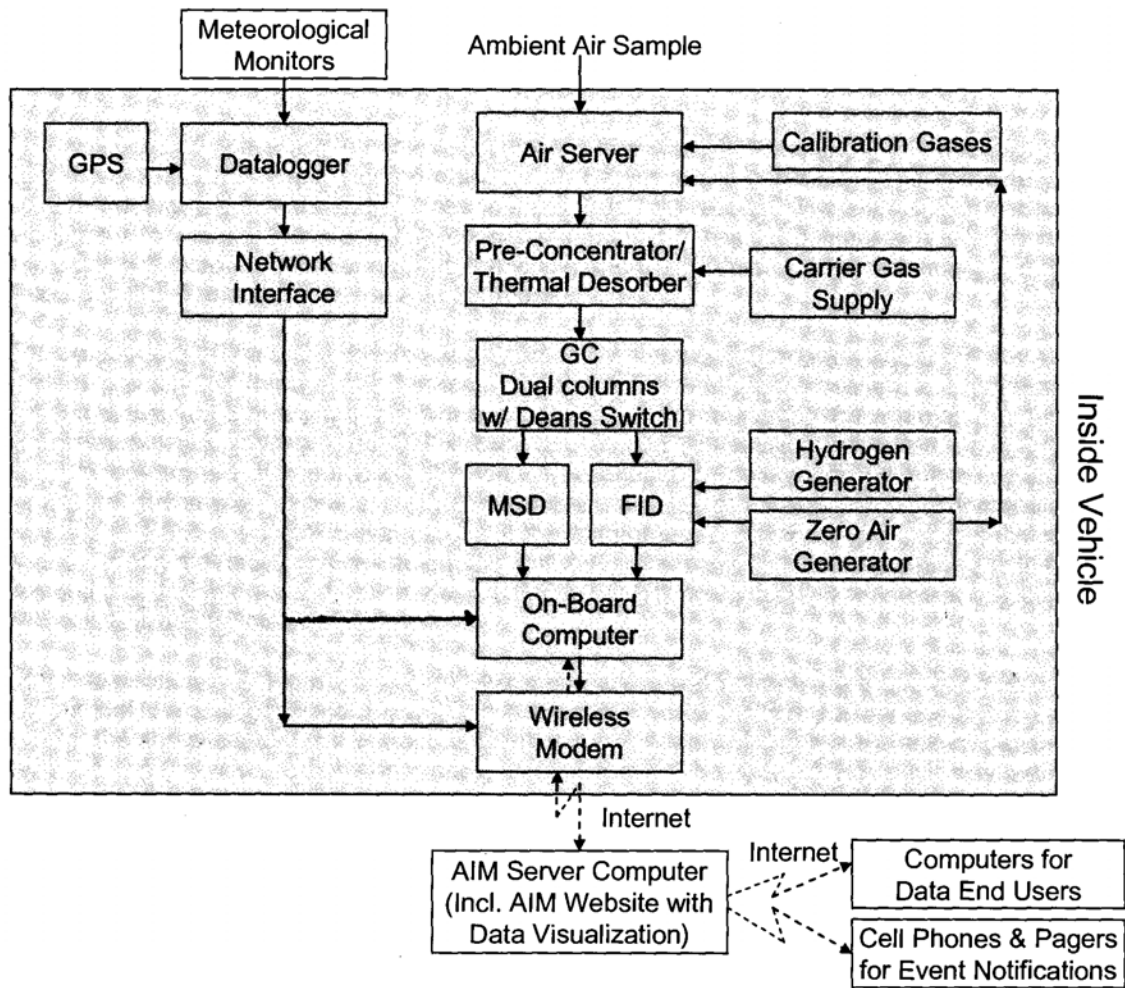


Figure 1. Sample path

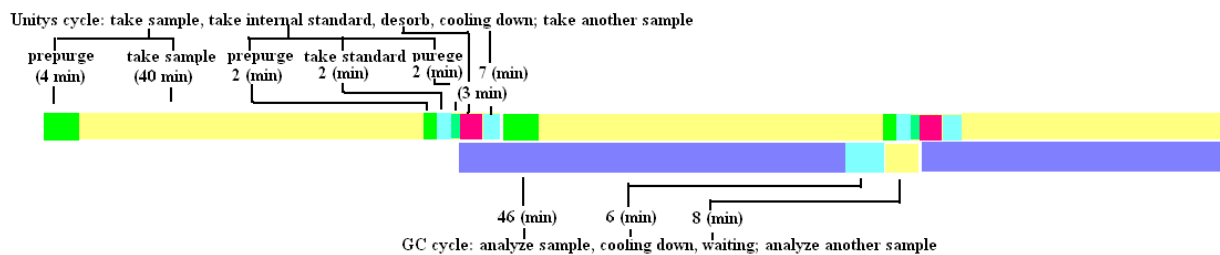
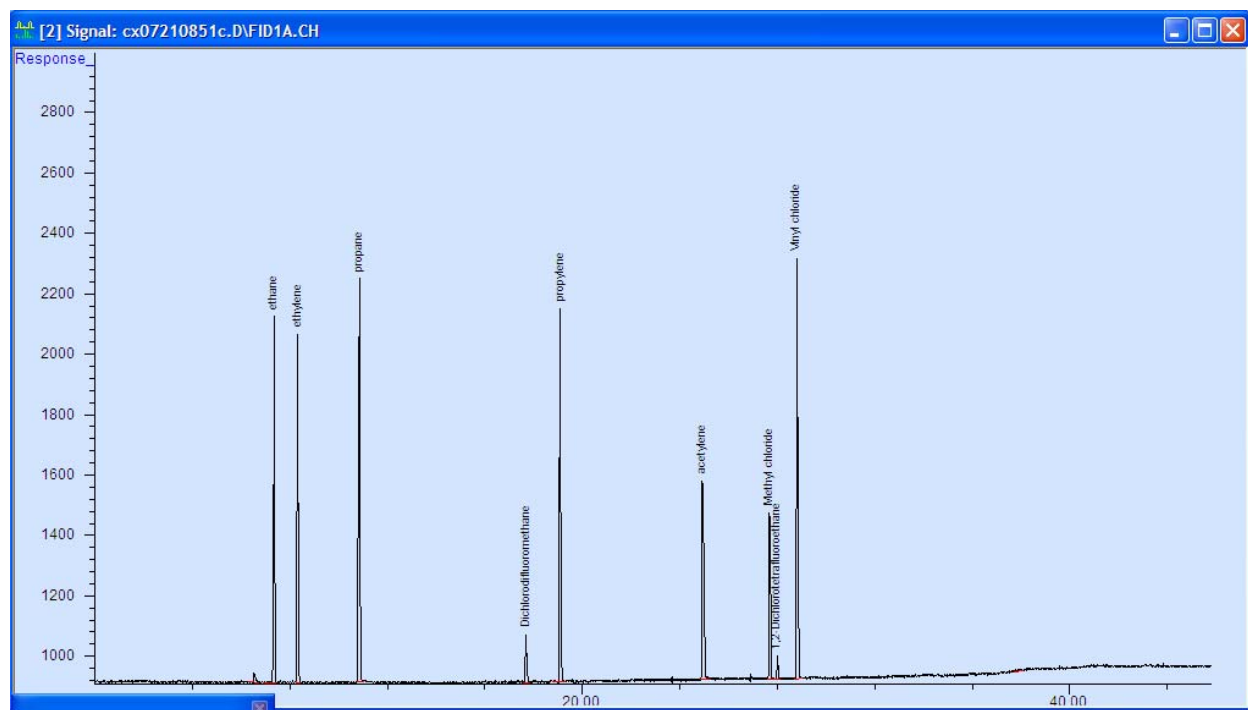
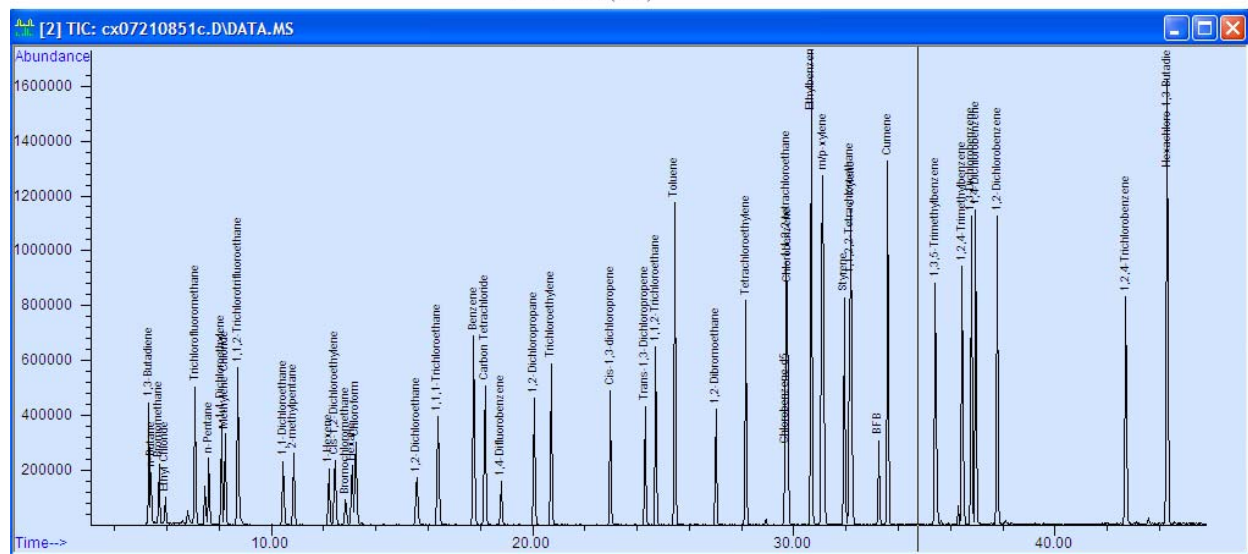


Figure 2. GS/MS and Unity cycle chart



Plot Column (FID)



BP1 Column (MS)

Figure 3 Elution sequences for PLOT Column and BP1 clolumn

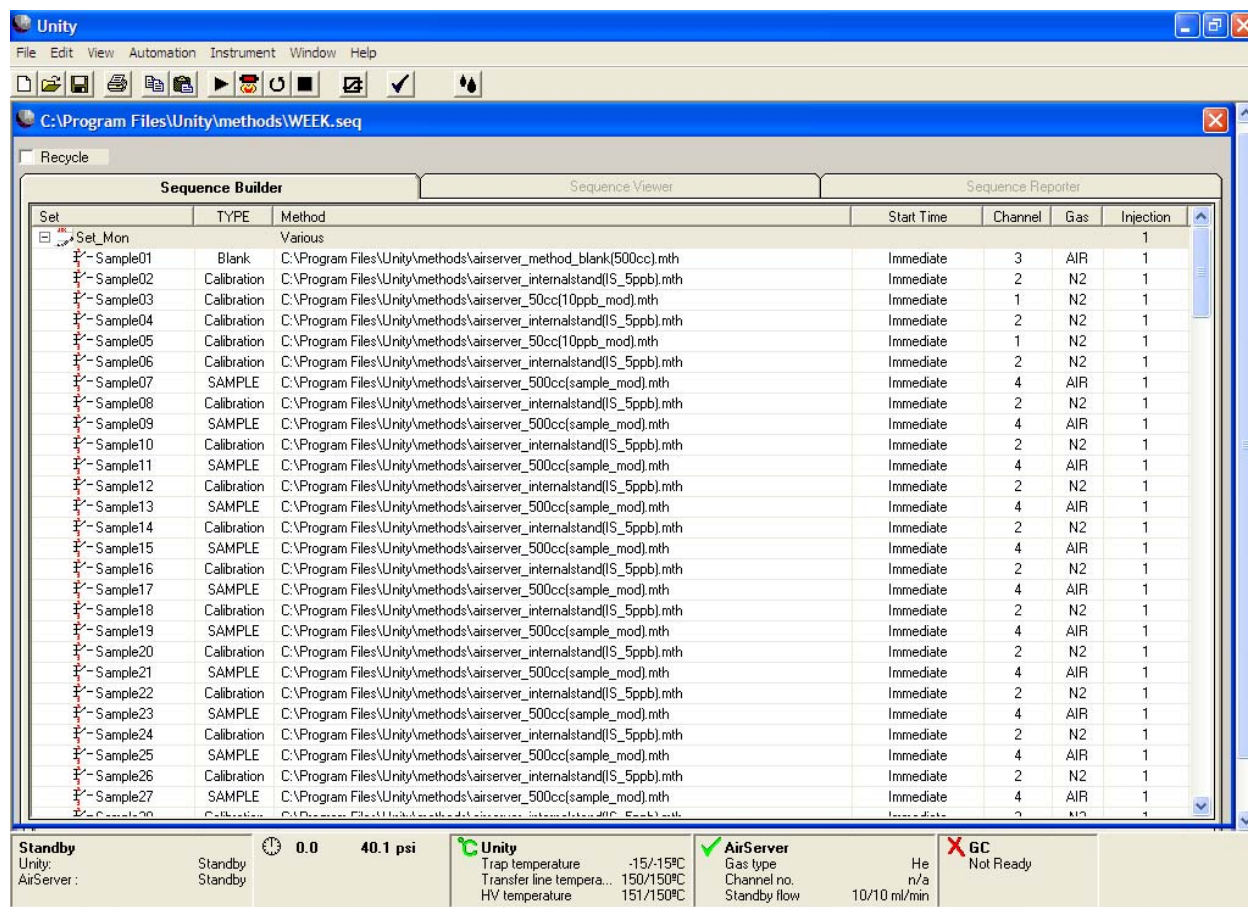


Figure 4 Control sequence for UNITY

Unity

File Edit View Automation Instrument Window Help

C:\Program Files\Unity\methods\airserver_500cc(sample_mod).mth

On Line Air Standby Flow Rate ml/min
☒ Split On 10.0

Purge
 4.0 Prepurge Time 1.0 Trap Purge Time 20.0 Flow Rate ml/min

On Line Sampling
 Sample Time 40.0 ☒ Pump On
 Flow Rate ml/min 12.5 ☒ Dryer On
☐ Leak test

Trap Desorb
 Trap Low -15 Trap Hold 0.0 ☒ Split On
 Trap High -15 Trap Heating Rate °C/s MAX Split Flow ml/min 10.0

150 Flow Path Temp
 0.0 GC Cycle Time
 5.0 Minimum Carrier Pressure

C:\Program Files\Unity\methods\airserver_50cc(10ppb_mod).mth

On Line Air Standby Flow Rate ml/min
☒ Split On 10.0

Purge
 4.0 Prepurge Time 2.0 Trap Purge Time 20.0 Flow Rate ml/min

On Line Sampling
 Sample Time 5.0 ☐ Pump On
 Flow Rate ml/min 10.0 ☒ Dryer On
☐ Leak test

Trap Desorb
 Trap Low -15 Trap Hold 0.0 ☒ Split On
 Trap High -15 Trap Heating Rate °C/s MAX Split Flow ml/min 10.0

150 Flow Path Temp
 0.0 GC Cycle Time
 5.0 Minimum Carrier Pressure

C:\Program Files\Unity\methods\airserver_method_blank(500cc).mth...

On Line Air Standby Flow Rate ml/min
☒ Split On 10.0

Purge
 4.0 Prepurge Time 2.0 Trap Purge Time 30.0 Flow Rate ml/min

Permitted Range = 0.0 <-> 99.9

On Line Sampling
 Sample Time 40.0 ☒ Pump On
 Flow Rate ml/min 12.5 ☒ Dryer On
☒ Leak test

Trap Desorb
 Trap Low -15 Trap Hold 0.0 ☒ Split On
 Trap High -15 Trap Heating Rate °C/s MAX Split Flow ml/min 10.0

150 Flow Path Temp
 0.0 GC Cycle Time
 5.0 Minimum Carrier Pressure

C:\Program Files\Unity\methods\airserver_internalstand(1S_5ppb).mth

On Line Air Standby Flow Rate ml/min
☒ Split On 20.0

Purge
 2.0 Prepurge Time 1.0 Trap Purge Time 20.0 Flow Rate ml/min

On Line Sampling
 Sample Time 2.0 ☐ Pump On
 Flow Rate ml/min 12.5 ☒ Dryer On
☐ Leak test

Trap Desorb
 Trap Low -15 Trap Hold 3.0 ☒ Split On
 Trap High 310 Trap Heating Rate °C/s MAX Split Flow ml/min 10.0

150 Flow Path Temp
 0.1 GC Cycle Time
 5.0 Minimum Carrier Pressure

Standby
 Unity: Standby
 AirServer: Standby

0.0 40.1 psi

Unity
 Trap temperature -15/-15°C
 Transfer line tempera... 150/150°C
 HV temperature 151/150°C

AirServer
 Gas type He
 Channel no. n/a
 Standby flow 10/10 ml/min

GC
 Not Ready

Figure 5 Methods for Unity

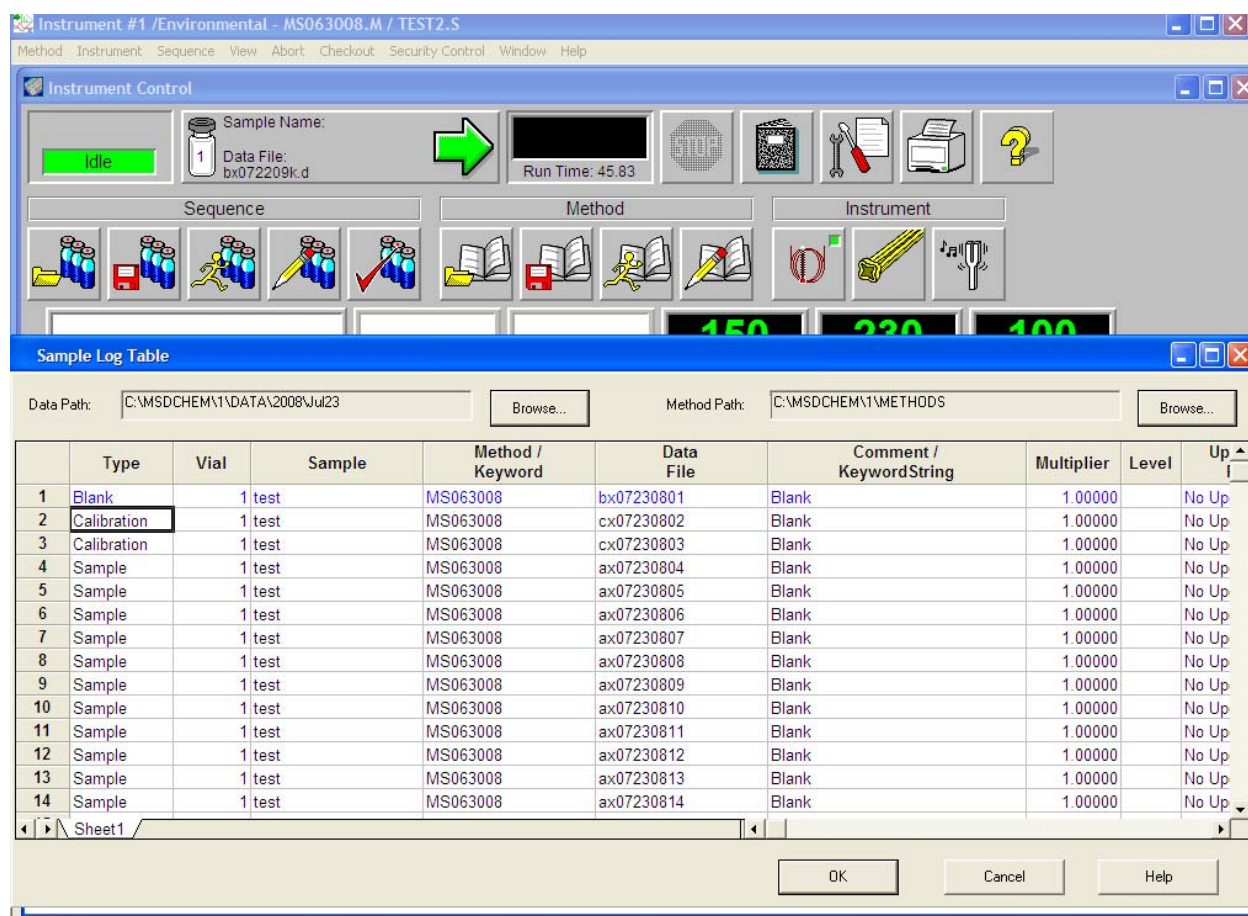


Figure 6 Control sequence for GC/MS

Appendix A: Sample Canister Data Sheet and Chain of Custody



City of Houston Bureau of Air Quality Control Canister Sampling Data Sheet and Chain-of-Custody



Sample ID:	Canister #: 1665
------------	------------------

Canister Cleaning Information (Laboratory Personnel Only)		
Canister Cleaning Operation	Pressure	Initials / Date
Canister Cleaned and Evacuated	29.0 in Hg	
Media Blank Evacuation	in Hg	

Sampling and Analysis Request Information (BAQC Investigator Only)		
Canister Received: (Initials / Date)	Canister Pressure (Upon Receipt): in Hg	
Pre-Sampling Pressure: -30 in Hg	Pre-Sampling Leak Test (Circle) Pass / Fail	
(* If the difference is greater than ± 2 in Hg, do not use the canister for sampling)		
Start Time: 1:02	End Time: 1:08	Elapsed Time: 30 seconds
Post-Sampling Pressure: -8 in Hg		
Potential Source (s) (Company's Name): CES	Potential Source (s) (Company's) Address (es): 4904 Griggs	
Sample Collection Address: 6002 Grace LN	Alleged Chemical (s) (If Known)	
GPS Coordinates: N29°41.833' W095°20.598'	Weather Conditions: Clear	
Sample Collected By: NLY	Sample Date: 10/27/08	
Phone Number: 713-640-4200	E-mail:	
Site Description and Field Comments: 357 IPB		

Analysis Method Requested (Circle) VOC's by TO-15 / Other Describe:

Canister Leak Test Information (BAQC Mobile Lab Personnel Only)					
Canister Leak Test	Field Pressure (in Hg)	Lab Pressure (in Hg)	Difference in Pressure	Test Results (Circle)	Initials / Date
Final				Pass / Fail / NA	

Canister Preparation Information (BAQC Mobile Lab Personnel Only)				
Canister Preparation	Dilution 1	Dilution 2	Initials / Date:	
Pre-Dilution Pressure	-7.5 in Hg	psia		
Post-Dilution Pressure	15.1 psia	psia		
Dilution Factors	#1 2.85	#2		
Laboratory Comments:				

Chain of Custody	
Relinquished by: (Signature/Date)	Received by: (Signature/Date)
<i>[Signature]</i> 10/27/08 12:00	<i>[Signature]</i> 10/27/08 12:00
	<i>[Signature]</i> 10/29/08 12:00

Effective Date: 01/24/08

Appendix B: Sample Final Report

**Bureau of Pollution Control and Prevention
Department of Health and Human Service
City of Houston**

Mobile Ambient Air Monitoring Laboratory Analysis Report

Analytical Fractions	Sample ID	Canister No.	Reported	Approval Signature/Date
VOC		1664		

Table of Contents

- I. Case Narrative
- II. Report Summaries
- III. Comments and Flag Definitions
- IV. Analytical Results
- V. Calibration and Quality Control Results
- VI. Batch Summaries

I. Case Narrative



City of Houston Bureau of Air Quality Control Canister Sampling Data Sheet and Chain-of-Custody



Sample ID:		Canister #: 1664	
Canister Cleaning Information (Laboratory Personnel Only)			
Canister Cleaning Operation	Pressure	Initials / Date	
Canister Cleaned and Evacuated		in Hg	
Media Blank Evacuation		in Hg	
Sampling and Analysis Request Information (BAQC Investigator Only)			
Canister Received: (Initials / Date)		Canister Pressure (Upon Receipt): 29.0 in Hg	
Pre-Sampling Pressure: -39 in Hg		Pre-Sampling Leak Test (Circle) Pass / Fail	
(* If the difference is greater than ± 2 in Hg, do not use the canister for sampling)			
Start Time: 11:36	End Time: 11:36	Elapsed Time: 35 seconds	
Post-Sampling Pressure: -9 in Hg			
Potential Source (s) (Company's Name):		Potential Source (s) (Company's) Address (es):	
		Ambient Air Sample	
Sample Collection Address: Church Grace W 66029		Alleged Chemical (s) (If Known)	
GPS Coordinates: N 29° 41.797' W 095° 20.615'		Weather Conditions: Clear SE	
Sample Collected By: NLY		Sample Date: 10/22/08	
Phone Number: 713-640-4200		E-mail:	
Site Description and Field Comments: Winds SE			

Analysis Method Requested (Circle) VOC's by TO-15 / Other Describe:

Canister Leak Test Information (BAQC Mobile Lab Personnel Only)					
Canister Leak Test	Field Pressure (in Hg)	Lab Pressure (in Hg)	Difference in Pressure	Test Results (Circle)	Initials / Date
Final				Pass / Fail / NA	

Canister Preparation Information (BAQC Mobile Lab Personnel Only)			
Canister Preparation	Dilution 1	Dilution 2	Initials / Date:
Pre-Dilution Pressure	-7.7 in Hg psia	psia	
Post-Dilution Pressure	15.0 psia	psia	
Dilution Factors	#1 2.87	#2	
Laboratory Comments:			

Chain of Custody	
Relinquished by: (Signature/Date)	Received by: (Signature/Date)
<i>[Signature]</i> / 10/22/08	<i>[Signature]</i> 10/22/08 15:15
<i>[Signature]</i> 10-27-08 11:43	<i>[Signature]</i> 10/27/08 11:43
<i>[Signature]</i> 10-27-08 16:48	<i>[Signature]</i> 10/27/08 17:00

Effective Date: 01/24/08

II. Report Summaries

Client Name	BPCP		
Sample ID			
Canister No.	1664		
Date & Time Collected	10/22/08 11:36		
Date & Time Received	10/27/08 17:00		
Date & Time Prepared	10/30//08 12:00		
Prepared Batch ID			
Pre-Sample Pressure (in Hg)	-28.8		
Pre-Dilution Pressure (in Hg)	-7.7		
Post-Dilution Pressure (Psi)	15.0		
Dilution Factor	2.87		
Date & Time Analyzed	10/30/08 17:18		
Analysis Batch ID	Canister103008		
Hold Time Spec (Days)	Prepare	Spec	30
		Actual	1
	Analysis	Spec	30
		Actual	8
Analytical Fraction	HR-VOC		
Lab Sample ID	Canister1664_103008		
Sample Matrix	Air		
Method Citation	TO15 Ambient		
Method Description	VOC Ambient GC/FID/MS		

III. Comments and Flag Definitions

Standard Data Qualifiers

Flag	Definition
B	Analyte detected in method blank and concentration > 0.5 ppbv
I	Interference or coelution suspected
NA	Not analyzed/Not available
ND	Not detected at the specified reporting limit
Q	Result does not meet specification
U	Result less than sample specific method detection limit

Analyst Comments

Sample Condition Comments

IV. Analytical Results

Sample ID	
Canister No.	1664
Lab Sample ID	Canister1664_103008
Instrument data files	
Date & Time Prepared	10/30/08 12:00
Pre-Sample Pressure (in Hg)	-28.8
Pre-Dilution Pressure (in Hg)	-7.7
Post-Dilution Pressure (Psi)	15.0
Dilution Factor	2.87
Date & Time Analyzed	10/30/08 17:18
Analysis Batch ID	Canister103008
Sample Matrix	Air
% Moisture	NA
Instrument	GC/FID/MS
Units	ppbv

Parameter	CAS No.	Concentration	Flag	MDL
Ethane	74-84-0	4.8		0.3
Ethylene	74-85-1	1.2		0.3
Propane	74-98-6	2.9		0.4
Dichlorodifluoromethane	75-71-8	N.D.		2.2
Propylene	115-07-1	0.9		0.4
Acetylene	74-86-2	0.6		0.3
Methyl chloride	74-87-3	N.D.		0.9
1,2-Dichlorotetraflu...	76-14-2	N.D.		1.1
Vinyl chloride	75-01-4	0.5		0.4
1,3-Butadiene	106-99-0	0.3	U	1.0
n-Butane	106-97-8	1.3		0.5
Bromomethane	74-83-9	0.6	U	0.7
Ethyl Chloride	75-00-3	N.D.		0.7
Trichlorofluoromethane	75-69-4	0.6		0.4
n-Pentane	109-66-0	0.7		0.4
1,1-Dichloroethylene	75-35-4	0.3	U	0.4
Methylene Chloride	75-09-2	1.2	B	0.8
1,1,2-Trichlorotrifluo...	76-13-1	0.4	U	1.0
1,1-Dichloroethane	75-34-3	0.5		0.5
2-Methylpentane	107-83-5	0.4		0.4
1-Hexene	592-41-6	0.2	U	0.4
Cis-1,2-Dichloroethylene	156-59-2	0.5	U	0.9
Hexane	110-54-3	0.2		0.2
Chloroform	67-66-3	0.4	U	1.5
1,2-Dichloroethane	107-06-2	0.5	U	1.0
1,1,1-Trichloroethane	71-55-6	0.3	U	1.8
Benzene	71-43-2	1.1		0.5
Carbon Tetrachloride	56-23-5	0.4	U	2.4
1,2-Dichloropropane	78-87-5	0.3	U	1.4
Trichloroethylene	79-01-6	0.5	U	0.6
Cis-1,3-dichloropropene	10061-01-5	0.3	U	1.2
Trans-1,3-Dichloropropene	10061-02-6	0.4	U	0.6

1,1,2-Trichloroethane	79-00-5	0.4	U	0.7
Toluene	108-88-3	1.0		0.5
1,2-Dibromoethane	106-93-4	0.6		0.6
Tetrachloroethylene	127-18-4	0.7	U	0.8
1,1,1,2-Tetrachloroethane	630-20-6	0.5		0.5
Chlorobenzene	108-90-7	0.9		0.4
Ethylbenzene	100-41-4	0.5		0.4
m/p-Xylene	108-38-3 & 106-42-3	0.0	U	0.8
Styrene	100-42-5	0.9		0.4
o-Xylene	95-47-6	0.4		0.2
1,1,2,2-Tetrachloroethane	79-34-5	0.5	U	0.9
Cumene	98-82-8	0.3	U	0.4
1,3,5-Trimethylbenzene	108-67-8	0.3	U	0.3
1,2,4-Trimethylbenzene	95-63-6	0.4		0.4
1,3-Dichlorobenzene	541-73-1	1.5	B	0.3
1,4-Dichlorobenzene	106-46-7	1.5	B	0.2
1,2-Dichlorobenzene	95-50-1	1.3	B	0.5
1,2,4-Trichlorobenzene	120-82-1	3.4	B	1.2
Hexachloro-1,3-Butadiene	87-68-3	1.5	B	0.9

Surrogate Compound	% Recovery	Limits	Flag
BFB(Bromofluorobenzene)	81.1	70-130	

V. Calibration and Quality Control Results

Daily calibration results

Sample Type	Daily Calibration
Analysis batch ID	Calibration
Instrument data file	curve102908bp3b
Date & Time Analyzed	10/30/08 5:24
Instrument	GC/FID/MS
Units	ppbv

Parameter	Reference Value	Measured Conc	% Recovery	Flag	QC Limits
Ethane	11.0	N.A.			70-130
Ethylene	11.0	N.A.			70-130
Propane	11.0	N.A.			70-130
Dichlorodifluoromethane	9.0	9.8	109		70-130
Propylene	11.0	N.A.			70-130
Acetylene	11.0	N.A.			70-130
Methyl chloride	9.0	9.5	105		70-130
1,2-Dichlorotetraflu...	8.6	9.3	108		70-130
Vinyl chloride	9.1	9.7	107		70-130
1,3-Butadiene	10.0	8.0	80		70-130
n-Butane	11.0	N.A.			70-130
Bromomethane	9.1	8.5	94		70-130
Ethyl Chloride	9.0	8.1	90		70-130
Trichlorofluoromethane	9.2	8.4	91		70-130
n-Pentane	11.0	N.A.			70-130
1,1-Dichloroethylene	11.0	9.2	84		70-130
Methylene Chloride	11.0	10.1	91		70-130
1,1,2-Trichlorotrifluo...	11.0	10.2	93		70-130
1,1-Dichloroethane	11.0	10.5	95		70-130
2-Methylpentane	11.0	N.A.			70-130
1-Hexene	11.0	N.A.			70-130
Cis-1,2-Dichloroethylene	11.0	9.9	90		70-130
Hexane	11.0	N.A.			70-130
Chloroform	11.0	10.8	98		70-130
1,2-Dichloroethane	11.0	10.7	97		70-130
1,1,1-Trichloroethane	11.0	9.8	89		70-130
Benzene	11.0	8.7	79		70-130
Carbon Tetrachloride	11.0	9.7	89		70-130
1,2-Dichloropropane	11.0	8.8	80		70-130
Trichloroethylene	11.0	8.4	76		70-130
Cis-1,3-dichloropropene	11.0	8.3	76		70-130
Trans-1,3-Dichloropropene	11.0	8.2	74		70-130
1,1,2-Trichloroethane	11.0	9.0	82		70-130
Toluene	11.0	9.7	88		70-130
1,2-Dibromoethane	11.0	9.8	89		70-130
Tetrachloroethylene	11.0	9.4	85		70-130
1,1,1,2-Tetrachloroethane	11.0	10.1	92		70-130
Chlorobenzene	11.0	10.5	95		70-130

Ethylbenzene	11.0	10.2	93		70-130
m/p-Xylene	22.0	19.9	91		70-130
Styrene	11.0	9.0	81		70-130
o-Xylene	11.0	9.6	87		70-130
1,1,2,2-Tetrachloroethane	11.0	9.6	87		70-130
Cumene	11.0	9.6	87		70-130
1,3,5-Trimethylbenzene	11.0	9.2	83		70-130
1,2,4-Trimethylbenzene	11.0	8.8	80		70-130
1,3-Dichlorobenzene	11.0	9.0	82		70-130
1,4-Dichlorobenzene	11.0	9.1	83		70-130
1,2-Dichlorobenzene	11.0	9.0	82		70-130
1,2,4-Trichlorobenzene	11.0	8.4	77		70-130
Hexachloro-1,3-Butadiene	11.0	9.3	84		70-130

Surrogate Compound	% Recovery	Limits	Flag
BFB(Bromofluorobenzene)	83.5	70-130	

Mass Spectrometer Tune

Mass/Energy	Ion Abundance Criteria		% Relative Abundance	Pass or Fail
	Lower Limit	Upper Limit		
50	8.0	40.0	25.7	Pass
75	30.0	66.0	58.2	Pass
95	100.0	100.0	100.0	Pass
96	5.0	9.0	6.7	Pass
173	0.0	2.0	1.4	Pass
174	50.0	120.0	68.5	Pass
175	4.0	9.0	7.9	Pass
176	93.0	101.0	94.9	Pass
177	5.0	9.0	6.2	Pass

Method Blank Results

Sample Type	Blank
Analysis batch ID	Canister103008
Matrix	Air
Instrument data file	BX103008a
Date & Time Analyzed	10/30/08 14:16
Instrument	GC/FID/MS
Units	ppbv

Parameter	CAS No.	Concentration	Flag	MDL
Ethane	74-84-0	N.D.		0.1
Ethylene	74-85-1	N.D.		0.1
Propane	74-98-6	0.1		0.1
Dichlorodifluoromethane	75-71-8	N.D.		0.8
Propylene	115-07-1	0.2		0.1
Acetylene	74-86-2	N.D.		0.1
Methyl chloride	74-87-3	0.3		0.3
1,2-Dichlorotetrafluoro...	76-14-2	N.D.		0.4
Vinyl chloride	75-01-4	0.5		0.2
1,3-Butadiene	106-99-0	0.1		0.4
n-Butane	106-97-8	0.4		0.2
Bromomethane	74-83-9	N.D.		0.2
Ethyl Chloride	75-00-3	0.5		0.3
Trichlorofluoromethane	75-69-4	0.1		0.1
n-Pentane	109-66-0	N.D.		0.1
1,1-Dichloroethylene	75-35-4	0.1		0.1
Methylene Chloride	75-09-2	1.3	B	0.3
1,1,2-Trichlorotrifluoro...	76-13-1	0.1		0.3
1,1-Dichloroethane	75-34-3	0.1		0.2
2-Methylpentane	107-83-5	N.D.		0.1
1-Hexene	592-41-6	N.D.		0.1
Cis-1,2-Dichloroethylene	156-59-2	0.2		0.3
Hexane	110-54-3	N.D.		0.1
Chloroform	67-66-3	0.1		0.5
1,2-Dichloroethane	107-06-2	0.2		0.4
1,1,1-Trichloroethane	71-55-6	N.D.		0.6
Benzene	71-43-2	0.2		0.2
Carbon Tetrachloride	56-23-5	N.D.		0.8
1,2-Dichloropropane	78-87-5	0.1		0.5
Trichloroethylene	79-01-6	0.2		0.2
Cis-1,3-dichloropropene	10061-01-5	0.2		0.4
Trans-1,3-Dichloropropene	10061-02-6	0.2		0.2
1,1,2-Trichloroethane	79-00-5	0.2		0.3
Toluene	108-88-3	0.2		0.2
1,2-Dibromoethane	106-93-4	0.3		0.2
Tetrachloroethylene	127-18-4	0.4		0.3
1,1,1,2-Tetrachloroethane	630-20-6	N.D.		0.2
Chlorobenzene	108-90-7	0.4		0.1
Ethylbenzene	100-41-4	0.2		0.1

m/p-Xylene	108-38-3 & 106-42-3	0.4		0.3
Styrene	100-42-5	0.3		0.1
o-Xylene	95-47-6	0.2		0.1
1,1,2,2-Tetrachloroethane	79-34-5	0.2		0.3
Cumene	98-82-8	0.1		0.2
1,3,5-Trimethylbenzene	108-67-8	0.2		0.1
1,2,4-Trimethylbenzene	95-63-6	0.3		0.1
1,3-Dichlorobenzene	541-73-1	0.9	B	0.1
1,4-Dichlorobenzene	106-46-7	1.0	B	0.1
1,2-Dichlorobenzene	95-50-1	0.9	B	0.2
1,2,4-Trichlorobenzene	120-82-1	2.8	B	0.4
Hexachloro-1,3-Butadiene	87-68-3	1.0	B	0.3

Surrogate Compound	% Recovery	Limits	Flag
BFB(Bromofluorobenzene)	78.8	70-130	

Duplicated Calibration Sample Results

Sample Type	Duplicate Calibration Samples
Analysis batch ID	Calibration
Instrument data file	curve102908p3a, curve102908p3b
Date & Time Analyzed	10/29/08
Instrument	GC/FID/MS
Units	ppbv

Parameter	Reference Value	Calibration sample	Duplicate Calibration Sample	RPD*	Flag	QC Limits
Ethane	11.0	8.0	8.1	1.6		25
Ethylene	11.0	7.2	7.4	2.0		25
Propane	11.0	8.2	8.3	1.5		25
Propylene	11.0	8.3	8.5	2.9		25
Acetylene	10.0	21.6	20.9	3.4		25
1,3-Butadiene	9.8	7.8	8.0	1.8		25
Butane	11.0	9.4	9.9	4.7		25
Pentane	12.0	9.1	9.7	6.9		25
2-Methylpentane	12.0	8.7	9.5	9.0		25
1-Hexene	12.0	9.8	10.5	6.3		25
Hexane	12.0	8.0	8.4	4.3		25
Benzene	12.0	9.2	9.5	3.7		25
Toluene	11.0	11.2	9.8	13.0		25
Ethylbenzene	11.0	11.0	10.0	8.8		25
m&p-Xylene	7.3	5.7	5.2	9.5		25
Styrene	11.0	5.5	5.0	8.4		25
o-Xylene	3.7	2.5	2.4	7.8		25

* RPD = $2 \times 100 \times \frac{\text{abs}(\text{calibration} - \text{duplicate calibration})}{(\text{calibration} + \text{duplicate calibration})}$

Surrogate Compound	Calibration Sample	Duplicate Calibration Sample	Flag	Limits
BFB(Bromofluorobenzene)	88.0	86.9		70-130

VI. Batch Summaries

Air Server Sampling Report

Carrier Gas = He

Reporting Started on 10/30/2008 1:19:52 PM

Sample Name	Sample Channel	Sampling Start Time	Sampling End Time	Sample Type	Sample Volume	Maximum Flow	Minimum Flow
Sample09	3	10/30/2008 13:26	10/30/2008 14:06	Blank	494	60	10
Sample10	2	10/30/2008 14:12	10/30/2008 14:14	Calibration	25	29	9
Sample13	6	10/30/2008 14:26	10/30/2008 15:06	Channel6	493	34	9
Sample14	2	10/30/2008 15:13	10/30/2008 15:15	Calibration	25	27	6
Sample07	7	10/30/2008 15:26	10/30/2008 16:06	Channel7	492	30	7
Sample08	2	10/30/2008 16:13	10/30/2008 16:15	Calibration	25	29	7
Sample15	8	10/30/2008 16:27	10/30/2008 17:07	Channel8	493	32	8
Sample16	2	10/30/2008 17:14	10/30/2008 17:16	Calibration	25	26	6
Sample17	6	10/30/2008 17:27	10/30/2008 18:07	Channel6	493	32	8
Sample18	2	10/30/2008 18:14	10/30/2008 18:16	Calibration	25	27	7
Sample19	7	10/30/2008 18:28	10/30/2008 19:08	Channel7	492	32	8
Sample20	2	10/30/2008 19:15	10/30/2008 19:17	Calibration	25	27	6
Sample21	1	10/30/2008 19:29	10/30/2008 19:34	Calibration	50	21	5
Sample22	2	10/30/2008 20:15	10/30/2008 20:17	Calibration	25	30	3

The image displays a chromatogram analysis software interface with two main plots.

Top Plot: Gas Chromatogram
 Title: [2] Signal: Canister1664_103008.D\FID1A.CH
 Y-axis: Response (980 to 1260)
 X-axis: Time (0 to 40.00)
 Labeled peaks: ethane, propylene, butylene, and various alkanes.

Bottom Plot: Mass Spectrum
 Title: [2] TIC: Canister1664_103008.D\DATA.MS
 Y-axis: Abundance (0 to 180,000)
 X-axis: Time (0 to 40.00)
 Labeled peaks: Benzene, Toluene, Ethylbenzene, Propylbenzene, and various alkanes.



Appendix C: Sample Canister Data Sheet and Chain of Custody



City of Houston

Bureau of Pollution Control and Prevention



Tedlar Bag Sampling Data Sheet and Chain-of-Custody

Sampling Information		
Sample ID (Bar Code Number)		
Tedlar Sample Bag Size	L (liter(s))	Pump Sampling Rate {L/min (liter(s) per minute)
Start Time:	End Time:	Elapsed Time:
Potential Source (s) (Company's Name):		Potential Source (s) (Company's) Address (es):
Sample Collection Address:		Alleged Chemical (s) (If Known)
GPS Coordinates:		Weather Conditions:
Sample Collected By:		Sample Date:
Site Description and Field Comments:		
Chain of Custody		
Relinquished By: (Signature/Date/Time)	Received By: (Signature/Date/Time)	

Effective Date: 07/18/08

Appendix D: Tedlar Bag Sampling Equipment Illustration

APPENDIX A

Figure

FIGURE 1 - Tedlar Bag Sampling Apparatus

